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GRADY TRIPLETT
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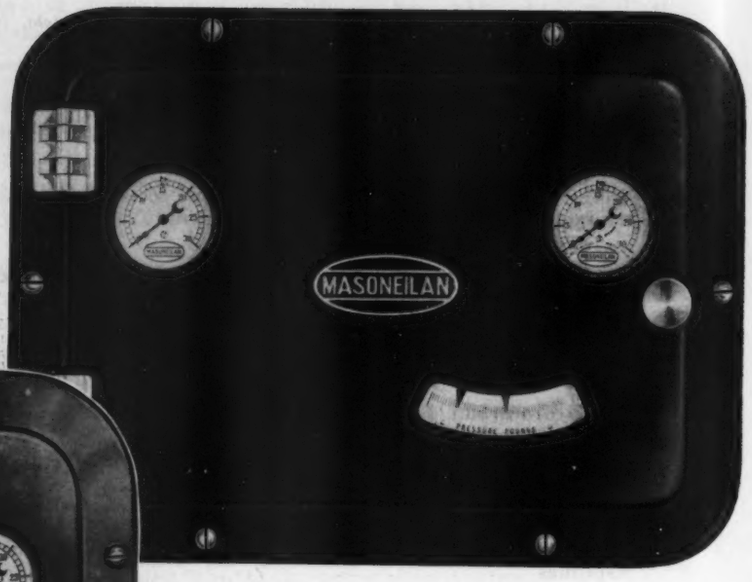

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Oil Demand Good But Holding Down of Gasoline Stocks Needed

By L. J. LOGAN

ALTHOUGH the oil industry's outlook is generally promising, in view of the current upswing of business, an important problem will be faced during the remainder of autumn and in the winter in holding gasoline stocks within reasonable proportions.

Fuel oils continue in comparatively large demand, and in meeting market requirements, the industry has been maintaining refinery runs at exceptionally high levels. Consequently, there has been relatively large production not only of the fuel oils but also of gasoline.

The inventories of gasoline therefore have not been brought into any better relation to requirements than in recent months, and they have prematurely commenced the usual fall-winter increase, despite the fact that economists regard the present stocks as at least 10,000,000 barrels larger than necessary.

While the large fuel oil demand is an important factor in promoting larger than desirable gasoline stocks, another important contributing factor in the past two months has been the failure of gasoline demand to measure up to expectations.

Lagging of gasoline demand has been reflected in the weekly statistics on gasoline production and gasoline stocks. Those figures have shown that in October, total demand for gasoline, domestic and export, was only about 2.5 percent greater than the demand in October of last year. That gain was below expectations. The Bureau of Mines had estimated that demand in October, 1939, would be 5.1 percent larger than that in October, 1938.

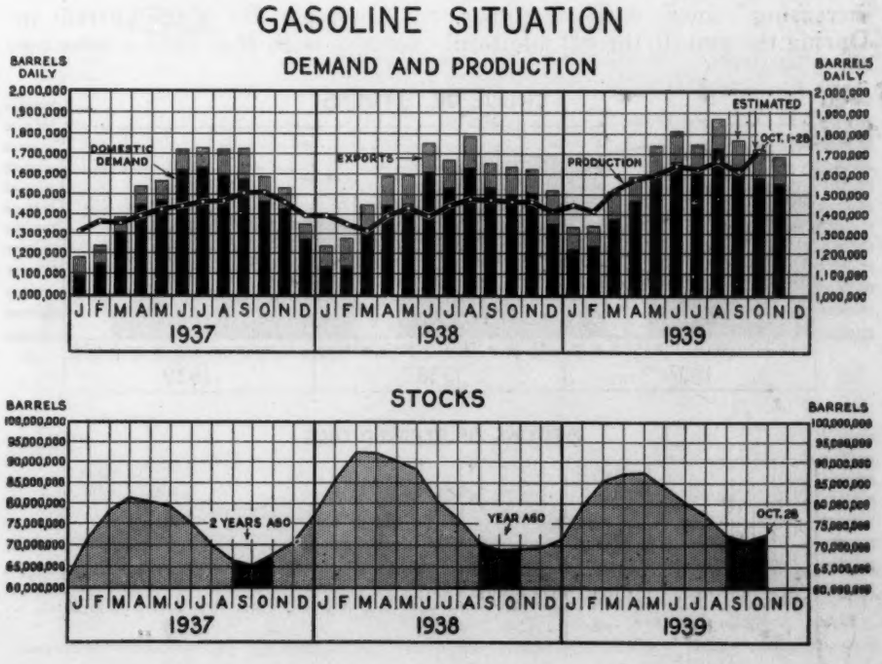
Whereas the gasoline demand averaged 1,638,600 barrels daily in October of last year, the Bureau of Mines estimated it would be 1,722,600 barrels daily, or 5.1 percent, higher in October of this year. But actually, the requirements apparently were only about 1,679,000 barrels daily. For in the four weeks from October 1 to October 28, gasoline production amounted to 48,508,000 barrels, as reported to the American Petroleum Institute; and that output was 1,492,000 barrels in excess of current demand, as evidenced by a net addition of that amount to storage in the meantime. The remaining 47,016,000 barrels, indicating market demand in the 28-day period, represented average requirements of 1,679,000 barrels daily.

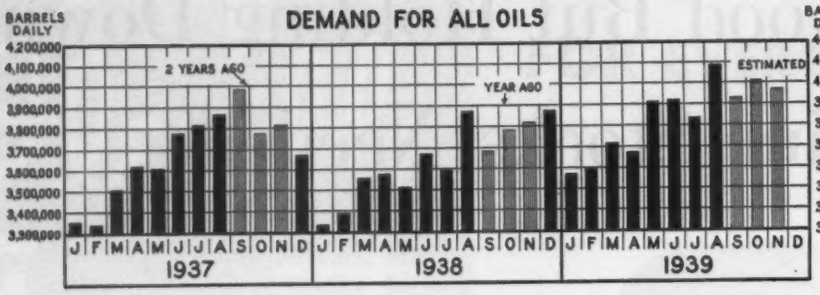
Similarly, gasoline demand had fallen below expectations in September, having been 4.8 percent greater than in September of last year, whereas the Bureau of Mines had forecast a 7.1 percent gain.

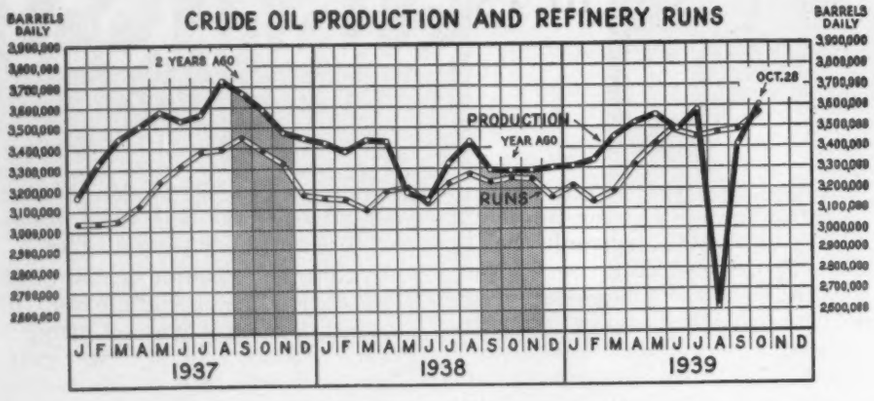
In contrast, gasoline demand had been larger than anticipated in August, having been 4.9 percent greater than in August of last year, whereas the Bureau of Mines had estimated an increase of only 3.3 percent.

Prospective Requirements

Despite much talk of possible increases in exports because of the European war and the high hopes arising from the present briskness of business, there is not in prospect so far any definite stepping up of gasoline demand. The Bureau of Mines has estimated that total demand for gasoline will be 3.9 percent larger in November, 1939, than in November, 1938, an increase







about in line with gains in past months. Domestic consumption is expected to show a 3.8 percent increase over a year ago, and the estimated exports of 3,900,000 barrels would be 5.5 percent larger than those of 3,698,000 barrels in November, 1938.

Stocks Increase Early

Although the industry usually continues to draw on gasoline stocks through October and into November, the large production at the refineries this fall has prevented such cutting down of the inventory, and the stocks have been gradually increasing since early October. During the month, the net addition was approximately 1,500,000 barrels, or at the average rate of about 50,000 barrels daily. The increase in the final week of the month was 538,000 barrels, or 77,000 barrels daily.

Having totaled 72,660,000 barrels on October 28, the national inventory of finished and unfinished gasoline was 5,070,000 barrels, or 7.5 percent, larger than that held on the corresponding date last year. The present stocks are regarded by economists as excessive by 10,000,000 barrels or more, in view of the current and prospective trends of consumption.

A comparison of the current inventory with that held a year ago reveals that the substantial gain for the United States has been due primarily to increases on the East Coast, in the Illinois region, on the Louisiana Gulf Coast, and in California, stocks being smaller in other districts. The following table shows the distribution of gasoline now and the changes that have been made since a year ago, by districts.

Region	Gasoline Stocks Oct. 29, 1938 (Barrels)	Gasoline Stocks Oct. 28, 1939 (Barrels)	Percent Change from Year Ago
East Coast	17,082,000	18,511,000	+ 8.4
Appalachian	2,802,000	2,611,000	— 6.8
Ind., Ill., Ky.	10,191,000	10,771,000	+ 5.7
Okla., Kans., Mo.	6,164,000	6,129,000	— 0.6
Inland Texas	1,523,000	1,495,000	— 1.9
Texas Gulf	9,930,000	9,539,000	— 4.0
Louisiana Gulf	2,202,000	2,554,000	+16.0
No. La.-Ark.	408,000	324,000	—20.6
Rocky Mt.	1,053,000	991,000	— 5.9
California	12,695,000	14,635,000	+15.3
Reported	64,050,000	67,560,000	+ 5.5
Estimated Unrep'rted	3,540,000	5,100,000	+44.1
Total U. S.	67,590,000	72,660,000	+ 7.5

First Eight Months

The increase in gasoline stocks over a year ago is not justified economically, despite the present larg-

Changes from Year Ago in Stocks of Crude Oils and Refined Oils in the United States

Barrels of 42 U. S. Gallons

LATEST WEEKLY DATA

(Sources: Crude Stocks, Bureau of Mines; all other figures, American Petroleum Institute)

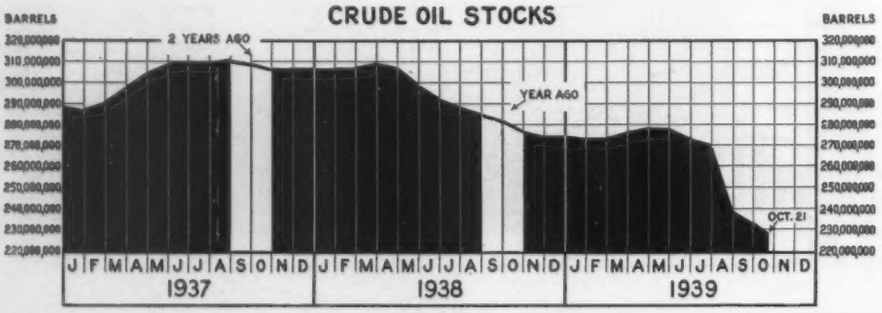
STOCKS OF:	Oct. 29, 1938	Oct. 28, 1939	Percent Change
Crude Oil	275,824,000	230,453,000	—16.4
Gasoline	67,590,000	72,660,000	+ 7.5
[2]Gas Oil & Distillate Fuels	32,739,000	31,073,000	— 5.1
[2]Residual Fuel Oil	120,540,000	109,781,000	— 8.5

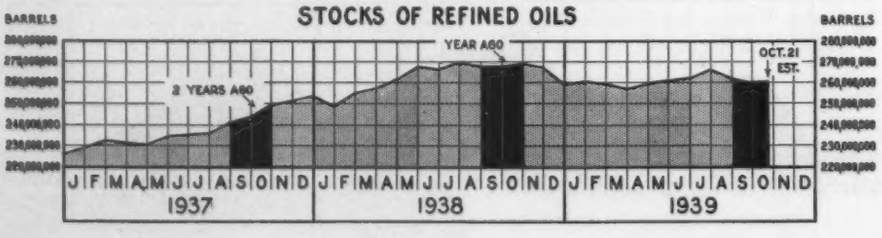
[1] At refineries only.
[2] At refineries only, except in California.

LATEST MONTHLY DATA

(Source: Bureau of Mines)

ITEM	Stocks at End of August 1938	1939	Percent Change
Summary			
Crude Petroleum:			
Refinable in U. S	285,640,000	238,479,000	—16.5
Heavy in Calif.	17,575,000	14,253,000	—18.9
Natural gasoline	8,022,000	6,624,000	—17.4
Refined products	268,022,000	262,738,000	— 2.0
Total, all oils	579,259,000	522,094,000	— 9.9
Days' supply:			
August basis	150	128	—14.7
8 Mo. basis	163	138	—15.3
Products			
Gasoline:			
Finished	64,599,000	66,448,000	+ 2.9
Unfinished	6,363,000	5,887,000	— 7.6
Total	70,962,000	72,335,000	+ 1.9
Kerosene	10,149,000	9,361,000	— 7.8
[1]Gas Oil and Distillate Fuels	28,841,000	28,982,000	+ 0.5
[1]Residual Fuel Oils	100,431,000	95,897,000	— 4.5
Lubricants	7,969,000	7,069,000	—11.3
Wax (thousands of pounds)	134,103	108,173	—19.5
Coke (short tons)	650,600	682,000	+ 4.8
Asphalt (short tons)	566,400	529,500	— 6.4
Road Oil	948,000	985,000	+ 3.9
Miscellaneous	274,000	282,000	+ 2.9
Other Unfinished Oils	41,601,000	40,819,000	— 1.9





Somewhat Less Favorable Gasoline Demand Indicated by Latest Bureau of Mines Forecast

(Barrels)

MONTH	Total Demand for Domestic Crude	MOTOR FUEL DEMAND		
		Domestic	Export	Total
September:				
September, 1939, forecast	105,320,000	49,100,000	4,000,000	53,100,000
September, 1938, actual	102,029,000	46,058,000	3,528,000	49,586,000
Change from year ago	+3.2%	+6.6%	+13.4%	+7.1%
October:				
October, 1939, forecast	111,300,000	48,900,000	4,500,000	53,400,000
October, 1938, actual	107,528,000	46,272,000	4,526,000	50,798,000
Change from year ago	+3.5%	+5.7%	—0.6%	+5.1%
November:				
November, 1939, forecast	108,600,000	46,700,000	3,900,000	50,600,000
November, 1938, actual	102,717,000	44,991,000	3,698,000	48,689,000
Change from year ago	+5.7%	+3.8%	+5.5%	+3.9%

er consumption, as the stocks a year ago were excessive to the extent that they seriously depressed the gasoline market.

Demand Up Moderately

Furthermore, demand is not up in proportion to the gain in stocks. In the first 8 months of 1939, total demand for gasoline was 4.9 percent larger than in the corresponding period last year, with domestic use up 5.9 percent and exports down 8.2 percent. In August, latest month for which official figures are available, total demand for gasoline was up 4.9 percent from a year before, domestic requirements having been 6.4 percent larger and exports 10.8 percent lower.

Fuel Oil Situation

Whereas gasoline stocks are larger than economically desirable, the stocks of both light and heavy fuel oils are comparatively small in relation to current and prospective demand.

Some success was achieved in October in expanding stocks of heating oils, to better take care of the heavy requirements of winter. The inventory of gas oil and distillate fuels was increased about 1,500,000 barrels during the month, to a total of 39,562,000 barrels as of October 28. But that supply was 5.1 percent smaller than the inventory held on the corresponding date last year, whereas demand has been running from 10 to 15 percent higher this year than last year.

Requirements Larger

In the first 8 months of 1939, the total demand for gas oil and distillate fuels was 13.5 percent larger than that in the similar period of 1938. Domestic use was up 16 percent and exports were 4.3 percent larger. In August, the total demand was up 9.5 percent, with domestic use 4.9 percent larger and exports up 2.3 percent.

Brisk industrial activity has held down stocks of the heavy fuel oils, which are moderate. During October, the inventories of the residual fuel oils were reduced about 700,000 barrels. The supply of 114,786,000 barrels on hand October 28 was 8.5 percent smaller than that held on the corresponding date last year, although demand has been around 10 percent better this year than last year.

Total demand for residual fuel oil in the first 8 months of 1939 was 10.4 percent larger than in the similar period of last year, domestic use having been 10.7 percent larger and exports 6.4 percent greater. The total demand in August was 9.1 percent larger than a year previously, with domestic requirements 9.9 percent greater and exports up 3.2 percent.

Both Domestic and Foreign Demand for Most Petroleum Products Running Higher This Year Than Last Year

Figures indicate barrels and are from Bureau of Mines

ITEM	AUGUST			FIRST 8 MONTHS		
	1938	1939	Percent Change	1938	1939	Percent Change
SUMMARY						
Total Demand	119,902,000	126,894,000	+ 5.8	865,995,000	921,098,000	+ 5.6
Daily average	3,868,000	4,093,000	+ 5.8	3,564,000	3,791,000	+ 5.6
Exports:						
Crude petroleum	7,003,000	5,969,000	— 14.8	54,430,000	48,222,000	— 11.4
Refined products	10,763,000	11,529,000	+ 7.1	78,060,000	80,034,000	+ 2.5
Domestic Demand:						
Motor fuel	50,459,000	53,728,000	+ 6.5	342,687,000	362,454,000	+ 5.9
Kerosene	4,292,000	4,436,000	+ 3.3	34,798,000	38,208,000	+ 9.8
Gas oil and distillate fuels	7,847,000	8,229,000	+ 4.9	71,080,000	82,586,000	+ 16.0
Residual fuel oils	23,665,000	26,012,000	+ 9.9	186,134,000	205,998,000	+ 10.7
Lubricants	2,002,000	1,963,000	— 1.9	13,750,000	14,998,000	+ 9.1
Wax	81,000	73,000	— 9.9	721,000	603,000	— 16.3
Coke	473,000	844,000	+ 76.8	3,485,000	4,638,000	+ 25.0
Asphalt	3,201,000	3,532,000	+ 10.3	15,936,000	17,131,000	+ 7.5
Road oil	1,581,000	1,576,000	— 0.3	5,575,000	5,914,000	+ 7.8
Still gas	5,753,000	5,925,000	+ 3.0	41,751,000	43,883,000	+ 5.1
Miscellaneous	158,000	211,000	+ 33.8	1,207,000	1,506,000	+ 24.8
Losses	2,624,000	2,867,000	+ 9.3	16,381,000	14,923,000	— 8.9
Total domestic demand	102,136,000	109,396,000	+ 7.1	733,505,000	792,842,000	+ 8.1
Daily average	3,295,000	3,529,000	+ 7.1	3,019,000	3,263,000	+ 8.1
TOTAL DEMAND FOR PRODUCTS						
Motor Fuel:						
Domestic	50,508,000	53,728,000	+ 6.4	342,687,000	362,454,000	+ 5.9
Exports	4,829,000	4,308,000	— 10.8	33,023,000	31,288,000	— 8.2
Total	55,337,000	58,036,000	+ 4.9	375,710,000	393,742,000	+ 4.9
Kerosene:						
Domestic	4,292,000	4,436,000	+ 3.4	34,798,000	38,208,000	+ 9.8
Exports	604,000	841,000	+ 39.4	4,890,000	5,340,000	+ 9.2
Total	4,896,000	5,277,000	+ 7.8	39,688,000	43,548,000	+ 9.7
Gas Oil and Distillate Fuels:						
Domestic	7,847,000	8,229,000	+ 4.9	71,080,000	82,586,000	+ 16.0
Exports	2,733,000	3,361,000	+ 2.3	21,219,000	22,136,000	+ 4.3
Total	10,580,000	11,590,000	+ 9.5	92,299,000	104,722,000	+ 13.5
Residual Fuel Oils:						
Domestic	23,665,000	26,012,000	+ 9.9	186,134,000	205,998,000	+ 10.7
Exports	1,667,000	1,613,000	+ 3.2	11,398,000	12,134,000	+ 6.4
Total	25,332,000	27,625,000	+ 9.1	197,532,000	218,132,000	+ 10.4
Lubricants:						
Domestic	2,002,000	1,963,000	— 1.9	13,750,000	14,998,000	+ 9.1
Exports	800,000	1,204,000	+ 50.5	6,457,000	7,484,000	+ 15.9
Total	2,802,000	3,167,000	+ 13.0	20,207,000	22,482,000	+ 11.2
Wax (thousands of pounds):						
Domestic	22,619	20,503	— 9.4	201,666	168,422	— 16.5
Exports	13,883	14,673	+ 5.7	116,997	156,286	+ 33.6
Total	36,502	35,176	— 36.4	318,663	324,708	+ 1.9
Coke (short tons):						
Domestic	94,500	168,800	+ 78.5	697,000	927,700	+ 33.0
Exports	13,100	25,400	+ 94.0	81,000	173,800	+113.0
Total	107,600	194,200	+ 80.5	778,000	1,101,500	+ 41.5
Asphalt (short tons):						
Domestic	582,100	642,200	+ 10.5	2,897,800	3,114,600	+ 7.5
Exports	1,900	3,300	+ 73.5	32,100	30,100	— 6.2
Total	584,000	645,500	+ 10.5	2,929,900	3,144,700	+ 7.3
Road Oil:						
Domestic	1,581,000	1,576,000	— 0.3	5,575,000	5,914,000	+ 7.8
Miscellaneous:						
Domestic	158,000	211,000	+ 33.6	1,207,000	1,506,000	+ 24.8
Exports	5,000	4,000	— 20.0	73,000	60,000	— 17.8
Total	163,000	215,000	+ 32.0	1,280,000	1,566,000	+ 22.4

New Thermofor Kiln and Clay-Regeneration Process for

Maintaining Decolorizing Clays at High Efficiencies

T. P. SIMPSON and J. W. PAYNE
Socony-Vacuum Oil Company, Paulsboro, N. J.

CONVENTIONAL burning methods for regenerating percolation filter clays result in rapid loss in decolorizing efficiency of the clays. Clays commonly are reduced to about 50 percent, or less, efficiency after 5 to 10 burns.

A new kiln, called the "Thermofor kiln," is described which is capable of maintaining clays at about fresh-clay efficiency after repeated regenerations. This kiln embodies features of temperature control and heat transfer which prevent the clays from reaching excessive temperatures. Clays which have been regenerated 16 times in a commercial unit of this type have been maintained at about 100 percent efficiency. This kiln is well suited also for regenerating clays by a method termed as "carbonization," whereby clays are obtained which show 150 to 300 percent efficiency for filtering solvent-refined oils.

The improved apparatus and processes described in this paper for regenerating and using decolorizing clays are controlled by patent rights assigned to the Socony-Vacuum Oil Company, Inc., and can be licensed by application to that company.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, at the Stevens Hotel, Chicago, Ill., November 16, 1939.

IN THE refining of mineral-oil products such as waxes, turbine and transformer oils, and particularly lubricants for internal-combustion engines and machinery, treatment by percolation through adsorptive substances such as clays is usually one of the most important operations. The purpose of this operation is to improve the color, color stability, odor, carbon residue, resistance to oxidation breakdown, and the demulsibility and, in the case of solvent-refined oils, to remove the last traces of solvent. Normally this operation is the final one conducted in finishing oils for markets.

Although many types of percolation adsorbents, such as bone char, silica gel, bauxite, and activated carbon, have been and still are employed extensively by the petroleum industry, the most common material in use today is fuller's earth. Fuller's earth is used so broadly throughout the petroleum industry today that the terms "fuller's earth" and "percolation clay" virtually are synonymous. Fuller's earth employed for this purpose is naturally active, has considerable compressive strength and hardness and, after tempering, is not disintegrated by water. It is most commonly applied in 30- to 60-mesh form; but 15-30, 20-90, 60-90, and other similar grades have found considerable use.

The yield of oil from a percolation filter depends to a large extent on the clay efficiency, the type of oil filtered, and the quality of product desired. In regular refinery practice the yields of finished oils from percolation cover a range of 5 to 150 barrels per ton of clay—the yields from used clays which have been regenerated more than five times in conventional burning equipment normally being only about half or less than half of those from fresh clays.

In the operation of a percolation filter when the oil produced is no longer of quality satisfactory for incorporation into the finished product, the filter is taken off stream. Preparations then are made for washing the spent percolator to remove the suspended oil, and to condition the spent clay so that it may be regenerated. The usual procedure for washing consists of leaching the clay with naphtha, and subsequently steaming to remove the residual naphtha and oil. These operations are carried out while the clay remains in the filter; and when they have been completed, the clay is ready for the final regeneration step required to remove the adsorbed tarry matter. The latter operation can be carried out in two radically different ways: by burning and roasting, or by extraction with solvents. Burning is the older method, and is used exclusively throughout the petroleum industry on the commercial scale—and it is with burning type of regeneration that this paper deals.

The equipment most commonly used for clay burning was adapted largely from ore-roasting machinery. An installation usually consists of either a rotary kiln, or a Wedge or Nichols-Herreshoff burner—the latter representing the multiple-hearth type, or a combination of several of these. An illustration of a Nichols-Herreshoff multiple-hearth furnace is shown in Figure 1. Conventional Wedge burners have a nominal capacity of about 120 tons per operating day, and Nichols-Herreshoff units normally run about 50 tons per day. A typical Wedge burner having a capacity of 5 tons per hour weighs about a million pounds, is about 25 feet in diameter by 25 feet in height, and has a burning-hearth area of about 1600 square feet. Typical present-day lubricating-oil refineries have a capacity of clay-burning equipment of from 40 to 300 tons per day, consisting of one or more of these types of burners.

Although rotary kilns have been used by many refiners, practically all installations since 1930 have

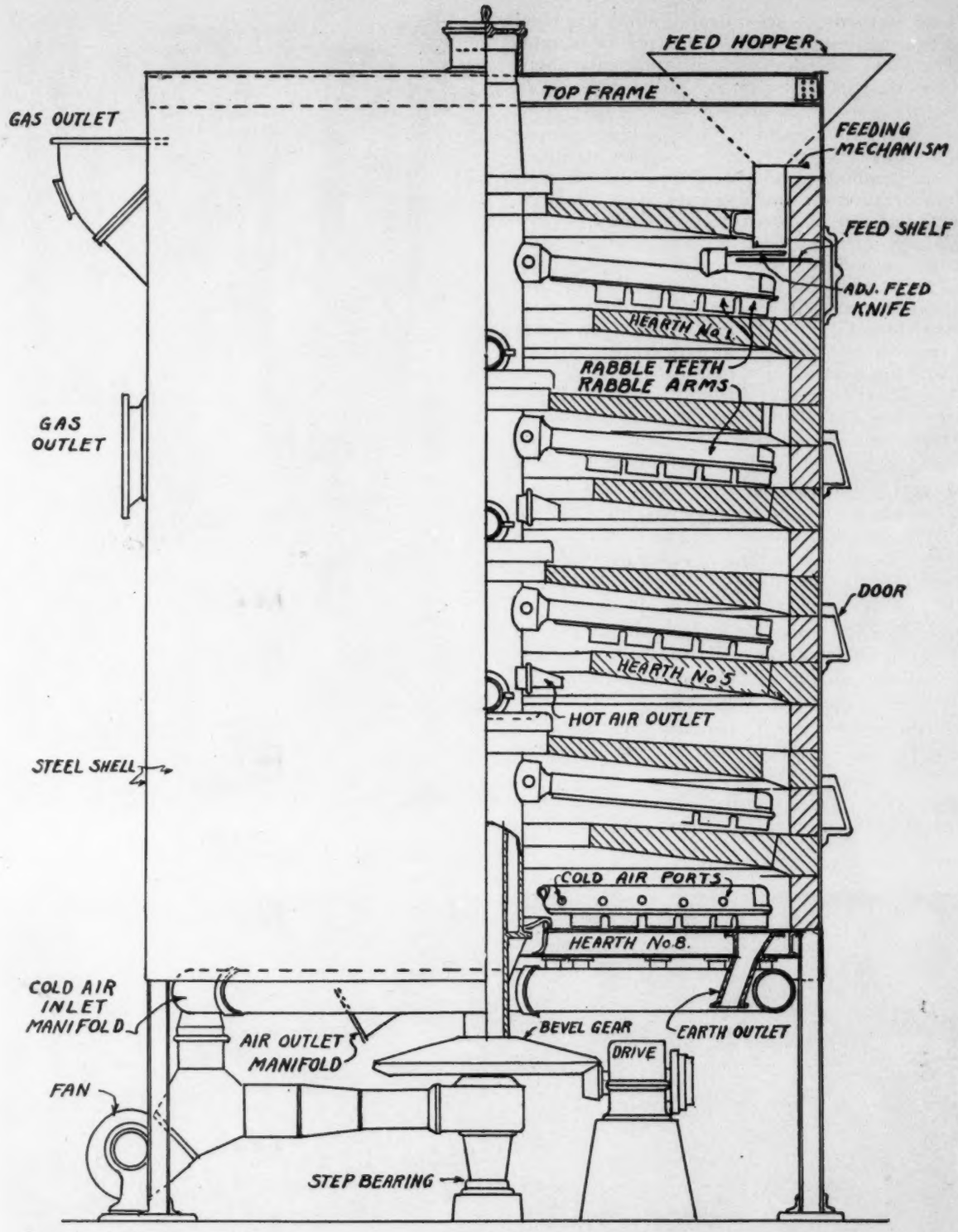


FIGURE 1
Nichols-Herreshoff Kiln.

been of the multiple-hearth type, and in many instances rotary units have been abandoned in favor of the latter.

In multiple-hearth burners the material to be burned passes down through successive hearths against a countercurrent stream of air. The apparatus has very little provision for heat removal or temperature control other than that manually obtained by the spraying of water or steam on the apparently overheated hearths. A reactivation of this type necessitates the addition of supplementary heat, which is supplied by flames over the hearths or in Dutch ovens. By such procedure the burning of the carbonaceous matter results in detrimental overheating of the clay. The life of the clay is shortened by incineration and, consequently, it is common practice to discard it after 6 to 10 burnings.

In view of the many deficiencies of multiple-hearth kilns—particularly the fact that they degrade clays rapidly due to overheating, thus increasing percolation costs enormously—the lubricating-oil refining industry long has needed and sought for improved

clay-burning methods. A great deal of effort has been expended toward improving the performance of multiple-hearth kilns, but due to their inherently poor temperature control, only minor gains have been made.

After a careful fundamental study of clay-burning methods it was evident that a properly-designed burner should embody means for the positive control of clay temperature and burning rate, with adequate provision for adding to or extracting heat from the system during operation. In view of the fact that an apparatus embodying these features had not been developed successfully, it was obvious that a new and novel approach would be required. It is the purpose of this paper to describe and submit to the petroleum industry the features, performance, operating characteristics, and application of a new clay-burning unit named the "Thermofor kiln," which has been developed on the basis of these requirements. This new unit embodies features of positive temperature control, burning rate, and heat transfer that make it suited admirably for the regeneration of percolation clays by treatment at high temperatures (900 to 1200° F.). The application of the Thermofor kiln is not restricted solely to handling of clays, as there are numerous uses to which it might be applied in other industries for the treatment of finely-divided solids under controlled conditions at high temperatures. In this respect the Thermofor kiln should find important commercial chemical-engineering applications beyond the scope of the petroleum industry.

The advantages of the Thermofor kiln over the conventional types of clay burners are summarized as follows:

1. Reactivation of clays to higher efficiencies and longer life than heretofore has been possible. This

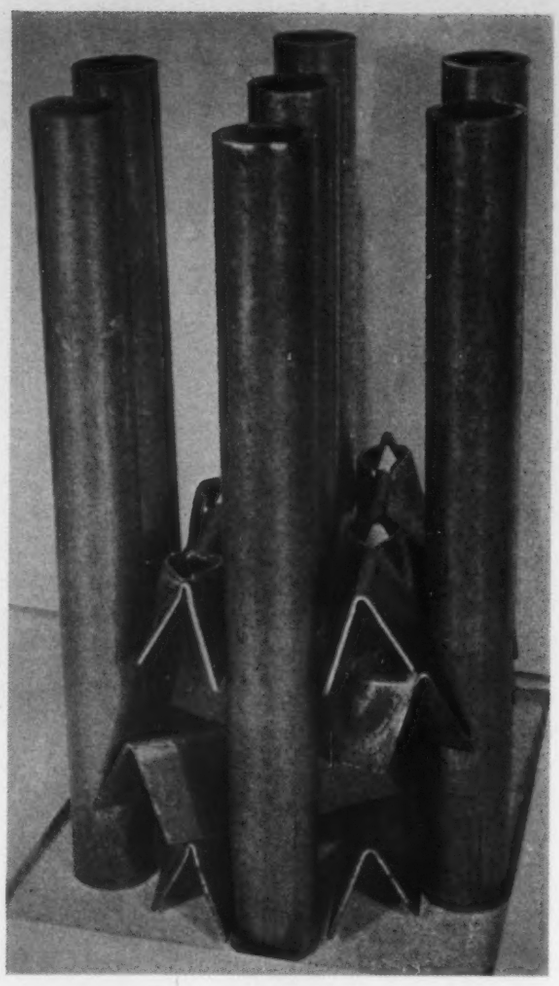


FIGURE 2
Tube and Angle Arrangement in Typical Thermofor Kiln.

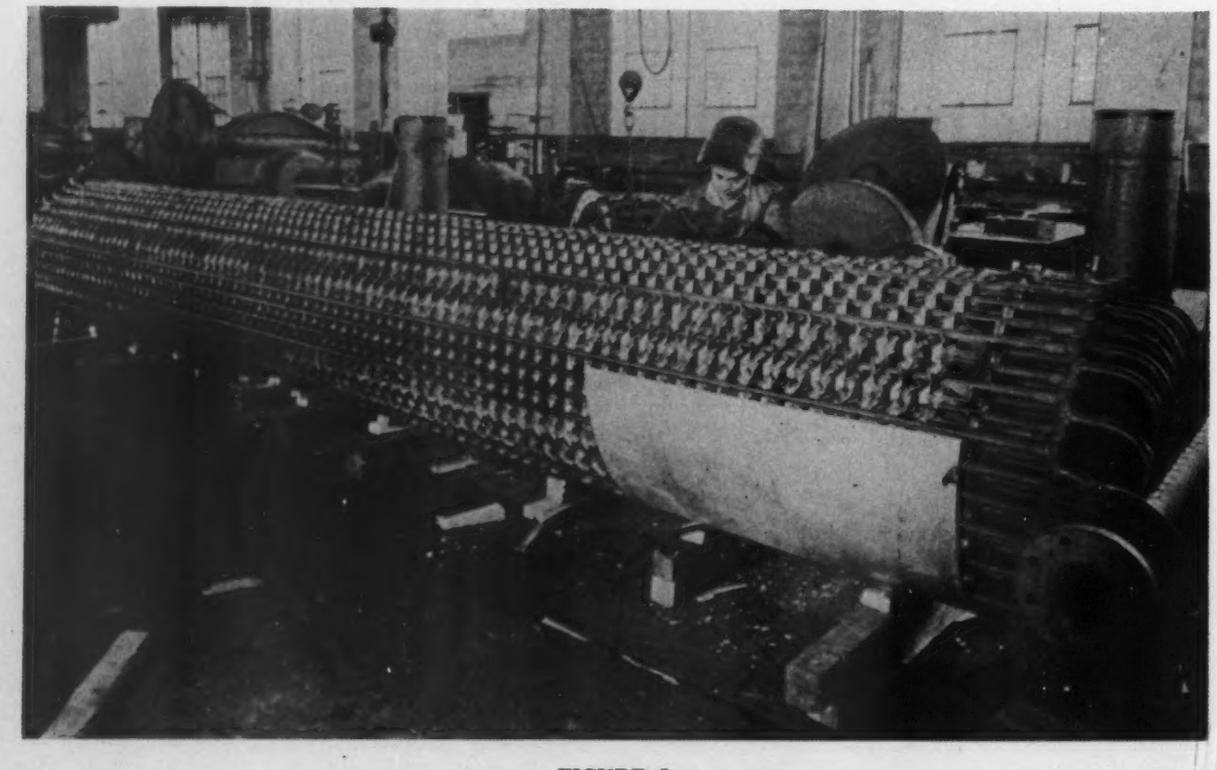


FIGURE 3
Tube and Angle Arrangement of Thermofor Kiln Proper

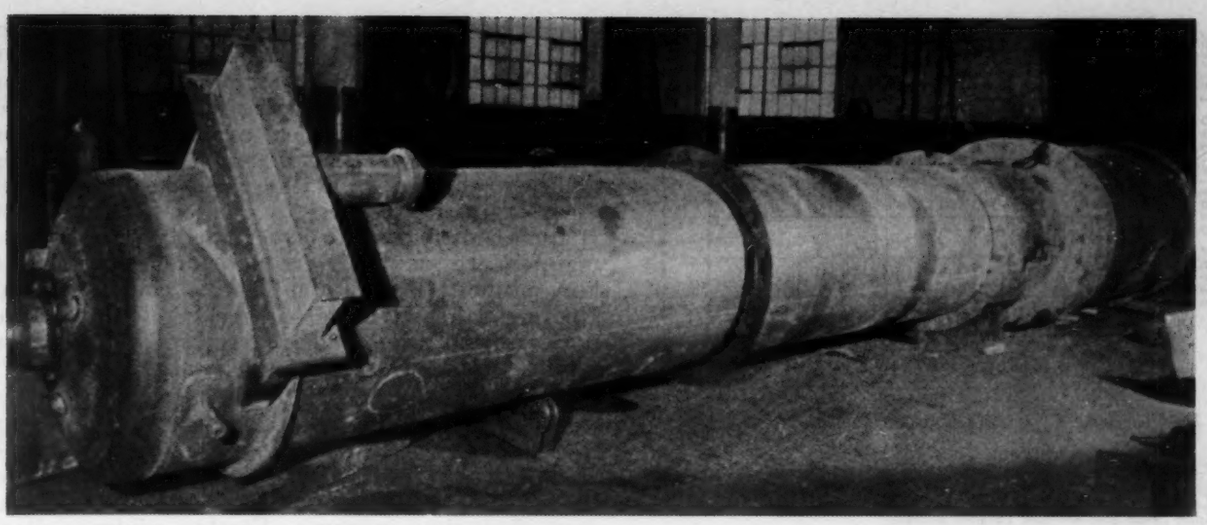


FIGURE 4
Assembled Thermofor for Kiln Ready for Installation

is accomplished by direct positive control of the burning temperature.

2. Low construction cost.
3. Low operating cost per ton of clay reactivated.
4. Excellent regeneration of clays by controlled partial combustion or "carbonization." Clays reactivated in this manner may be applied to distinct advantage in percolating solvent-refined oils. This type of regeneration is not practical with conventional types of clay burners.
5. Economical and practical clay burning on a comparatively small scale, particularly in plants in which clay is very expensive.
6. Ease of operation and reduced fire hazard.

The Thermofor kiln consists essentially of a stationary chamber containing vertical heat-transfer tubes, through which a heat-transfer medium flows. Figures 2, 3, 4, and 5 illustrate the general arrangement and layout of a Thermofor kiln. In normal practice for burning clays the heat-transfer medium would consist of molten metal or salt, and it would be maintained at 850 to 1150° F. The heat-transfer medium is pumped through the tubes to control the clay temperature by either removing or adding heat as needed. The heat-transfer tubes are surrounded by an interlaced structure of angle irons, which are stacked in such a manner that the tube bundle resembles a huge honeycomb of steel. These angle irons (see Figures 2 and 3) are stacked with their apexes pointing upward, and each angle is perforated with several ports to provide for the passage of air. The air ports of each angle are located so that they open directly under a closed area of an intercepting angle iron immediately above. The functions of the angles are: 1, to provide the required burning hearth surface; 2, to insure uniform clay flow through the kiln; 3, to provide air passages up through the clay; and, 4, to aid in the transfer of heat. A commercial Thermofor kiln of capacity of 50 tons per day weighs approximately 30,000 pounds, and has an equivalent burning-hearth area of 1800 square feet.

Reactivated percolation clays of greatly improved efficiencies have been produced consistently in both laboratory and plant development work. Many different types of experimental units—all involving similar principles of heat control—have been tested on the pilot-plant scale, with remarkably good results. A commercial unit of about 50 tons per day burning capacity now has been in continuous operation for nine months on clays used for percolating typical Pennsylvania stocks. Several batches of clay now have been burned 16 cycles in this unit, and their

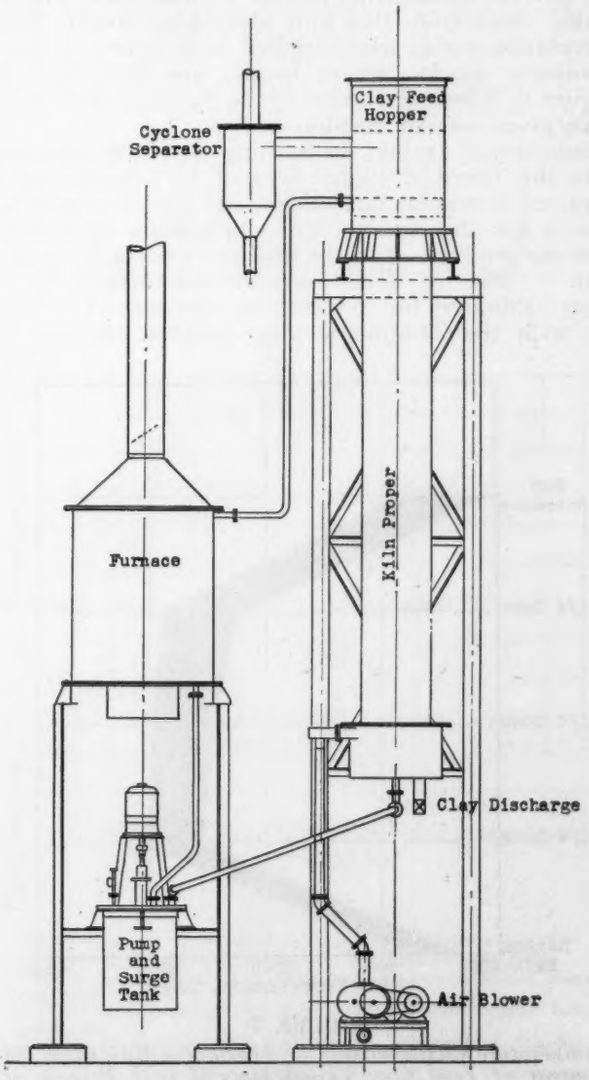


FIGURE 5
General Layout of Thermofor Kiln

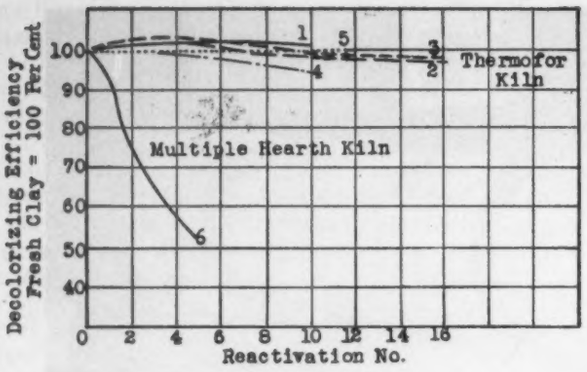


FIGURE 6

Decolorizing Efficiencies of Clays Reactivated by Burning in Commercial Kilns.

Curve 1—Laboratory percolations with Mid-Continent Duo-Sol-treated short residuum.

Curve 2—Plant percolations with Pennsylvania long and short residua, with and without chlorex treating.

Curve 3—Laboratory percolations as a check on plant percolations, *curve 2*.

Curve 4—Laboratory percolations with Mid-Continent acid-treated short residuum.

Curve 5—Laboratory percolations with acid-treated Coastal distillate.

Curve 6—Conventional operations on a variety of typical Pennsylvania stocks using plant-regenerated clays from a multiple-hearth kiln.

efficiency has been maintained at an average of about 100 percent during this period. Commercially regenerated clays from this unit also show similar high percolation yields when applied to a variety of Mid-Continent stocks. These results are illustrated in Figure 6. Numerous other cyclic burning operations have given similar results.

Substantial savings in burning costs are obtained with the Thermofor kiln: because no outside fuel is required in regular operations, and the air consumption is low due to excellent combustion conditions. The oxygen content of the flue gases normally is less than 1 percent. Fuel consumption—which is an appreciable item for conventional burners—is negligible with the Thermofor kiln, because the heat is obtained from burning of the adsorbed carbonaceous material. The only outside heat supplied is for bringing the burner up to temperature and for hardening of raw clays. Normally the heat needed is considerably less than the heat available from combustion of the carbonaceous material on the spent clay, and in some cases sufficient excess heat may be produced to justify recovery by auxiliary means. Another item contributing to lower operating costs is low maintenance, as there are no moving parts to the kiln proper. The 50-ton-per-day commercial unit mentioned hereinbefore showed no detectable wear nor corrosion, and required no repairs when inspected after six months' continuous operation.

As evidence of the close temperature control obtained with the Thermofor kiln, a chart is presented in Figure 7 which illustrates that the temperatures can be maintained within very narrow limits even when the nature of the clay feed is altered drastically over short-time intervals. Further evidence of this precise control is illustrated in Figure 8, which gives the actual operating-temperature curves for various clay zones in a kiln for a period of several hours during a full-scale commercial run.

As mentioned previously, the Thermofor kiln is an excellent type of apparatus for regenerating clays by controlled partial oxidation or other treatment at high temperatures. Such operations may involve partial removal of the tarry deposits from the clay by oxidation or with substantially no oxidation. For the sake of simplicity, this type of clay reactivation has been termed "carbonization," to distinguish it from regular methods in which a much greater degree of oxidation occurs. In carbonization it appears that the heavy hydrocarbon molecules present on the clay decompose, forming an active carbonaceous deposit which has remarkably good adsorption characteristics

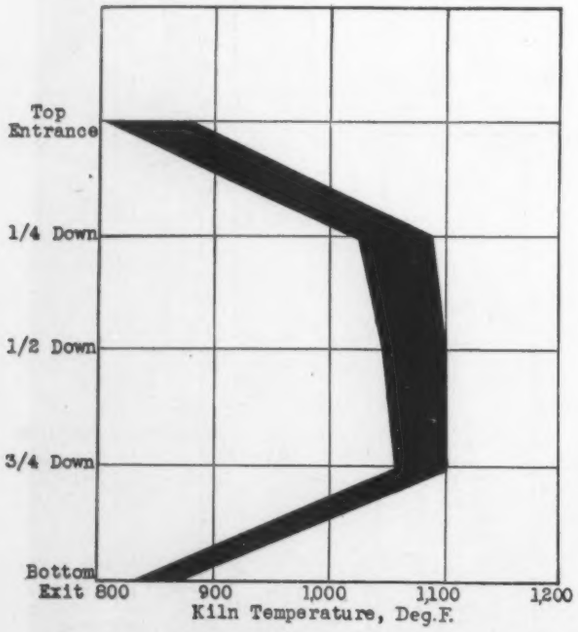


FIGURE 7

Temperature Characteristics of Thermofor Kiln when Oil Content of Feed Clay Varied from 0 to 5 Percent at 30-Minute Intervals with Clay Turnover in Kiln Once each Hour.

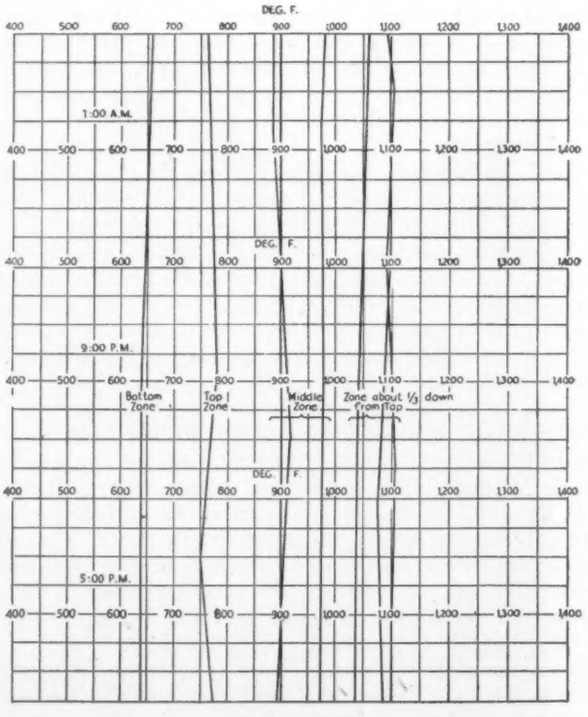


FIGURE 8

Temperature Chart of Commercial Thermofor Kiln with a Clay Rate of 21 Pounds Per Hour Per Cubic Foot of Kiln Volume and 7.2 Percent of Carbonaceous Material on Unburned Clay.

TABLE 1

Comparison of the Properties of Oils Percolated through Clays Regenerated by Various Methods

OIL STOCK	Clay No.	Method of Reactivation	Oxidation-Susceptibility Test*—Percent Volume of Sludge After: 5 Days	6 Days	11 Days	13 Days	14 Days
Mid-Continent Duo-Sol-treated long residuum	Fresh	Burning	10	14	.....	.....	.....
	7	Burning	6	10	.....	.....	.....
	3	Carbonization	.....	17	.....	.....	.....
	4	Carbonization	.....	10	.....	.....	.....
Mid-Continent Duo-Sol-treated short residuum	Fresh	Burning	.....	.....	Nil	Nil	Nil
	6	Burning	.....	.....	Nil	Nil	Trace
	5	Carbonization	.....	.....	Nil	Nil	Nil
	9	Carbonization	.....	.....	Nil	Nil	Trace
Pennsylvania Chlorex-treated neutral	Fresh	Burning	4	6	13	.....	.....
	4	Burning	5	8	15	.....	.....
	3	Carbonization	5	6	13	.....	.....
	4	Carbonization	4	5	11	.....	.....
Pennsylvania Chlorex-treated long residuum	Fresh	Burning	.....	.....	Nil	Nil	Tar
	2	Burning	.....	.....	Nil	Nil	Trace
	1	Carbonization	.....	.....	Nil	Nil	Nil
	2	Carbonization	.....	.....	Nil	Nil	Tar

			Carbon Residue	Sligh‡	Michie§	Brown-Boveri Turbine Test† Neutral No.	Sludge
			(Percent by Weight)				
Mid-Continent Acid-treated neutral	4	Burning	.....	21	.....	.....	.....
	4	Carbonization	.....	16	.....	.....	.....
	5	Carbonization	.....	18	.....	.....	.....
Coastal Acid-treated neutral	2	Burning	.....	.....	.....	10	0
	3	Burning	.....	.....	.....	26	0
	2	Carbonization	.....	.....	.....	11	0
	6	Carbonization	.....	.....	.....	14	0
Pennsylvania Chlorex-treated long residuum	Fresh	Burning	0.15	.....	.....	.....	.....
	2	Burning	0.18	.....	.....	.....	.....
	1	Carbonization	0.15	.....	.....	.....	.....
	2	Carbonization	0.14	.....	.....	.....	.....
Pennsylvania short residuum	Fresh	Burning	1.6	.....	.....	.....	.....
	4	Burning	1.3	.....	.....	.....	.....
	3	Carbonization	1.6	.....	.....	.....	.....
	5	Carbonization	1.3	.....	.....	.....	.....
Pennsylvania neutral	Fresh	Burning	.....	26	0.67	.....	.....
	4	Burning	.....	20	1.00	.....	.....
	2	Carbonization	.....	26	0.81	.....	.....
	6	Carbonization	.....	26	0.80	.....	.....

* Laboratory oxidation test at 350 deg. F. with air passing over surface of sample in a glass beaker. Sample is stirred with iron stirrer at constant rate.
† H. Staeger, "Brown-Boveri Test," Brown Boveri Rev. 16, 92-7 (1929).
‡ T. S. Sligh, Proc. Am. Soc. Testing Materials 27 (Part 1) 461 (1927).
§ A. C. Michie, Bull. 148 British Standards Institution, April (1933).

for certain color bodies. Steam, inert gases, or reduced amounts of air may be passed through the clay to purge it during carbonization. In general yields on a volume basis, for clay reactivated in this manner, compare favorably with fresh burned clays. For some oils, notably Duo-Sol-treated and other solvent-refined stocks, the yields from clays reactivated by carbonization are from two to four times as high as from the same clays which have had the carbonaceous matter burned completely. Discarded clays which have an efficiency of 50 percent, as compared with fresh clays, when regenerated in this manner will exhibit efficiencies nearly double that of fresh burned clay for filtering Duo-Sol-treated Mid-Continent stocks. With respect to solvent-refined oils, the high activity of clays reactivated by carbonization is not impaired to any marked extent with increased number of regenerations. Samples of clay reactivated in this manner 10 to 15 times exhibit efficiencies twice as high as those of freshly-burned clays. In many instances clays of 300 percent efficiency have been obtained. Curves illustrating the benefits of carbonizing operations are given in Figure 9.

Oils percolated through clays which have been reactivated by carbonization have almost identical properties to those filtered through completely-burned clays. Proof of this is apparent from Table 1.

In typical lubricating-oil decolorizing operations

(*Continued on page 76*)

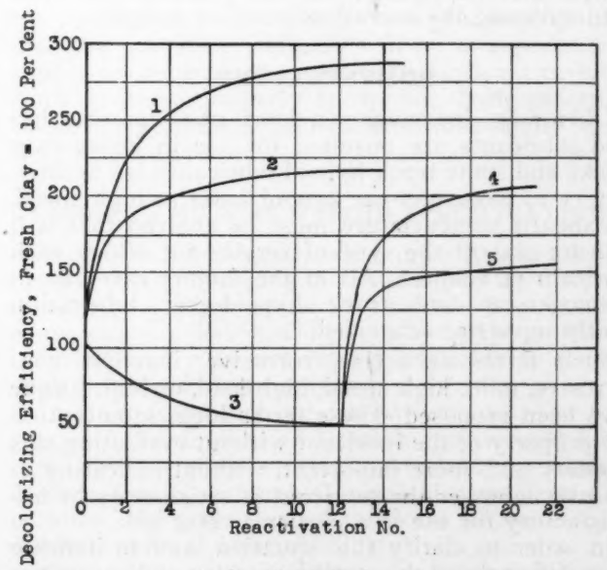


FIGURE 9

Efficiency of Clay Reactivated by Carbonization for Decolorizing Mid-Continent Duo-Sol-treated Oils.

Curve 1—Carbonized clay, Mid-Continent Duo-Sol-treated short residuum.

Curve 2—Carbonized clay, Mid-Continent Duo-Sol-treated long residuum.

Curve 3—Multiple-hearth burned clay, Mid-Continent Duo-Sol-treated long and short residua.

Curve 4—Carbonization cycles starting with No. 12 multiple-hearth clay, Mid-Continent Duo-Sol-treated short residuum.

Curve 5—Carbonization cycles starting with No. 12 multiple-hearth clay, Mid-Continent Duo-Sol-treated long residuum.

Hypoid-Lubricant Requirements

for Passenger Car and Truck Rear Axles

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THE recent use of hypoid gears in heavy-duty truck rear axles has introduced a new problem in hypoid-gear lubrication.

Truck hypoid gears do not differ fundamentally in design from passenger-car hypoid gears, but they operate under somewhat different service conditions and, therefore, may require a different type of lubricant to prevent scoring and scuffing of the gear-tooth surfaces.

A passenger-car hypoid-gear axle operates under the most severe lubrication conditions at high speed, whereas a heavy-duty-truck hypoid axle operates under the most severe lubrication conditions at low speed with maximum engine torque in low gear.

Hypoid gears have been used in passenger-car rear axles since 1926.[3] Prior to 1936 they were used by only a limited number of automobile manufacturers. The lubrication of these axles did not present a serious problem to the petroleum industry. Approved lubricants, largely of the lead-soap active-sulfur type, were handled by the authorized car dealers and service stations, and no attempt was made to market a hypoid lubricant through the filling stations.

In 1936 hypoid gears were adopted for quantity production by a large number of passenger-car manufacturers. This widespread use of hypoid-gear axles made it necessary quickly to expand the sources of supply for hypoid lubricants. The success of the whole program, and the almost complete absence of service failures or complaints was due to: 1, the extensive educational campaign carried out by both the automotive and petroleum industries; and 2, the cooperation of the petroleum industry in marketing a powerful extreme-pressure or hypoid lubricant through all retail lubrication outlets.

Lead-soap active-sulfur hypoid lubricants have been distributed widely, and have been used successfully in all makes of passenger-car hypoid-gear rear axles. These lubricants, when properly compounded, are stable under the operating conditions encountered in passenger cars, and afford a maximum factor of safety at high speed. As far as can be determined at the present time, the lead-soap active-sulfur lubricants will continue to be entirely satisfactory for all passenger-car hypoid-gear rear axles. The lead-soap active-sulfur lubricants are, however, unsatisfactory for use in heavy-duty truck hypoid-gear axles.

Conversely, some of the so-called mild types of hypoid lubricants are satisfactory in heavy-duty-truck hypoid-gear rear axles and in passenger-car hypoid-gear rear axles at low or moderate speeds, but fail to prevent scoring or scuffing of the ring-gear and pinion tooth surfaces in passenger-car service at high speed.

The problem of differentiating between passenger-car service and heavy-duty-truck service demands a prompt extension of the original educational program so that the owner, operator, dealer, and filling-station attendant will understand and appreciate the factors that affect the lubrication requirements of hypoid gears under these radically different service conditions.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, at the Stevens Hotel, Chicago, Ill., November 16, 1939.

THE hypoid gear was developed originally for passenger-car service to reduce gear noise.[3] Other inherent advantages of the hypoid gear,[3, 9] viz., offset of the pinion gear and greater tooth strength, have been utilized in recent passenger-car axle designs. These advantages have given the body engineer greater freedom in body design through the lowering of the propeller shaft and the reduction in axle size. Improved riding qualities also have resulted through the reduction in unsprung axle weight.

Indirectly, all of these advantages of the hypoid gear are retained in the truck axle. However, the controlling factor in the use of the hypoid gear in truck axles is the fact that for the same ring-gear diameter the tooth section is far stronger than the corresponding spiral-bevel-gear tooth section. From the gear engineer's viewpoint this increase in tooth strength makes it possible to design a smaller axle for a given power transmission, or to provide a substantial increase in factor of safety in axle life without increasing the overall axle size or weight.

NOMENCLATURE

Obviously, inasmuch as some passenger-car hypoid lubricants are unsuited for use in heavy-duty trucks and some truck hypoid lubricants are unsatisfactory in passenger-car hypoid axles at high speed, a standard nomenclature must be evolved that will indicate clearly the type of service for which each lubricant is adapted. All of the factors involved in passenger-car and truck hypoid-gear lubrication clearly must be recognized.

Such terms as active, corrosive, inactive, noncorrosive, mild, high speed, high load, or high torque have been proposed. These terms focus attention on one property of the lubricant without evaluating this property and, more important, without indicating to the user whether the lubricant is satisfactory or unsatisfactory for use in a particular rear axle.

In order to clarify this situation, and to indicate more definitely to the station operator and car owner the suitability of a particular lubricant for a specific use, a number of automobile manufacturers have adopted the following nomenclature:

"Passenger-car-duty hypoid lubricant," and
"Truck-duty hypoid lubricant."

The word "duty" was included in the nomenclature in order to emphasize the fact that the operating conditions, and not the type of vehicle alone, must be

considered in selecting a rear-axle lubricant. A light-duty commercial car or truck built on a passenger-car chassis, and operating essentially under passenger-car conditions, may require a "passenger-car-duty hypoid lubricant" rather than a "truck-duty hypoid lubricant."

Some lubricants may qualify as "truck-duty hypoid lubricants" for use in all heavy-duty hypoid-gear truck axles and as "passenger-car-duty hypoid lubricants" for use in certain passenger cars, but may be entirely inadequate for use in other passenger cars at high speed. Such lubricants could not be classified properly as "passenger-car-duty hypoid lubricants" for universal distribution and marketing in the passenger-car field.

UNIVERSAL OR DUAL-PURPOSE GEAR LUBRICANT

The need for simplifying recommendations for transmission and rear-axle lubrication, and the desirability of marketing fewer gear lubricants, have been presented in a number of technical papers,[2, 4] and have been discussed by the SAE sub-division on transmission and rear-axle lubricants.

A reduction in the number of gear lubricants required, obviously, will benefit the oil industry in eliminating unnecessary stocks and, from the automotive industries' viewpoint, minimize the possibility of confusion in the service field. A single gear lubricant may be the ultimate answer to the gear-lubrication problem; however, it must be remembered that such a lubricant cannot be a compromise, but must meet fully the lubrication requirements under all operating conditions in all units in which its use is recommended.

Applied specifically to the passenger-car and truck hypoid-axle problem, a universal or dual-purpose hypoid lubricant must lubricate properly all makes and models of passenger-car hypoid axles under the most severe high-speed driving conditions, and at the same time must lubricate satisfactorily all makes and models of heavy-duty-truck hypoid axles under the most severe operating conditions existing at low road speed with full torque through low gear.

A hypoid lubricant—even though it may be capable of lubricating a complete line of passenger-car and truck hypoid axles—produced by a single automotive manufacturer cannot be distributed universally as a dual-purpose hypoid lubricant unless it is also capable of lubricating all other makes of passenger-car and heavy-duty-truck hypoid axles under all service conditions.

MARKETING PROBLEM

Many refiners and marketers now carry three gear lubricants:

1. A mineral gear oil.
2. A mild extreme-pressure gear lubricant.
3. A powerful extreme-pressure or hypoid lubricant. Some refiners have discontinued the mineral gear oils in all except the heavier grade (SAE 250) used in spiral-bevel-gear heavy-duty-truck axles; and market, for general distribution, through the filling stations:

a. A mild extreme-pressure gear oil, for use in transmissions and in the older models of passenger cars equipped with spiral-bevel-gear axles.

b. A powerful extreme-pressure or hypoid lubricant for use in all passenger-car hypoid gear axles and in some passenger-car models equipped with highly-stressed spiral-bevel gears.

To those marketers who prefer to continue with either two or three gear lubricants, it would appear that two courses are open.

One solution would be to retain the present lead-soap active-sulfur lubricant as a "passenger-car-duty hypoid lubricant," and to modify the mild EP lubricant, now used as a transmission lubricant and as a rear-axle lubricant in some of the older models equipped with spiral-bevel gears, to make it suitable for both passenger-car transmissions and heavy-duty-truck hypoid rear axles. These modified lubricants could be classified as a "transmission and truck-duty hypoid lubricant," and in connection with the lead-soap active-sulfur "passenger-car-duty hypoid lubricant" would enable the car dealer and filling station adequately and safely to service all transmissions and rear axles.

The second solution would be to retain the present mild EP lubricant for use in transmissions and in spiral-bevel axles that do not require a hypoid lubricant, and to replace the present lead-soap active-sulfur hypoid lubricant with a lubricant that will lubricate satisfactorily all passenger-car and all truck hypoid axles under all operating conditions. This new lubricant could be classified both as a "passenger-car-duty hypoid lubricant" and as a "truck-duty hypoid lubricant."

However, it should be emphasized again that a lubricant intended for universal use in both passenger-car and truck hypoid axles cannot be a compromise, but must lubricate adequately and prevent scoring or scuffing of the gear-tooth surfaces in all makes and models of passenger cars and trucks under all operating conditions.

The automotive manufacturers are not attempting to direct the development along either line, or to specify the type or composition of hypoid lubricants for use in service. They are trying only to point out the problem as it affects their own products, in order that the petroleum industry will be in a position to supply to the trade the necessary lubricant or lubricants required properly to service both passenger cars and trucks under all field conditions under which they may be operated.

GENERAL MOTORS HYPOID SPECIFICATIONS

When the hypoid-gear axle originally was adopted by several car divisions of General Motors Corporation for production in the 1937 models, hypoid lubricants were not distributed generally by the petroleum industry, and were not readily available to the car dealers nor individual owners.

In order to protect the car owners and to provide adequate distribution of a satisfactory hypoid lubricant, the car divisions made available to General Motors dealers, through General Motors Parts Corporation, the same type of lubricant as was used in production for the initial filling.

This merchandising of hypoid lubricants was only a temporary expedient, and was discontinued by the corporation as soon as distribution was effected by the petroleum industry and hypoid lubricants became available to the dealers through their regular sources of supply. However, further to safeguard the car owner and dealer during this transition period, it was necessary to establish an approved list of hypoid lubricants.

As soon as laboratory tests could be correlated with performance in service, specifications were issued, and the approved lists were discontinued. The first group of specifications issued under date of July, 1937, covered the types of lubricants used by the car divisions for original servicing of passenger-car hypoid axles. These specifications, although intended primarily to cover factory purchases, were viewed by the trade in general as a recommendation for specific lubricants meeting these chemical and physical requirements, and a disapproval of all other types of lubricants regardless of their properties or service records. In order to correct this impression, and as it obviously was impossible to cover all future commercial developments, revised specifications—based entirely upon general requirements and axle-performance tests—were issued under date of July, 1939.

Par. 1 and 2 of this revision (July, 1939) constitute the complete specification for passenger-car hypoid lubricants. A lubricant meeting these requirements, regardless of composition, may be considered satisfactory for original filling or for use in service. The detailed chemical and physical requirements outlined under the individual specification numbers, as noted in Par. 3, cover specific types on which laboratory tests have been correlated with service performance. These detailed specifications are intended primarily as a convenience in inspecting lubricants purchased by the car divisions for initial filling. All of the types covered by the detailed chemical and physical specifications meet the minimum requirements of Par. 1 and 2, but they do not possess necessarily the same factor of safety under actual service conditions.

Lubricants meeting the requirements of the General Motors specifications, therefore, may be classified as "passenger-car-duty hypoid lubricants" for use in past and current models of General Motors passenger cars. However, as the lubrication requirements[9] of an axle depend upon the gear design and operating conditions, a specific lubricant—even though it meets the performance tests outlined in Par. 2, or one of the detailed chemical and physical specifications—may not be satisfactory in axles built by other automobile manufacturers. Each car manufacturer must formulate his own specifications, based entirely upon the lubrication requirements of his particular axle.

The General Motors specifications for hypoid lubricants (July, 1939) were issued before heavy-duty trucks employing hypoid axles were marketed by the corporation. However, preliminary tests indicate that several of the lubricants covered by these specifications may be classified also, insofar as current General Motors requirements are concerned, as "truck-duty hypoid lubricants," as well as "passenger-car-duty hypoid lubricants." Again these lubricants may be unsatisfactory in other makes of truck axles; and before a lubricant can be marketed for general distribution as either a "passenger-car-duty hypoid lubricant" or a "truck-duty hypoid lubricant," the lubricant manufacturer must assure himself that his lubricant or lubricants will function satisfactorily in all makes of either or both passenger-car and truck hypoid axles.

Although a "truck-duty hypoid lubricant" that also will qualify as a "passenger-car-duty hypoid lubricant" may offer a marketing advantage, it is not required that a lubricant which will perform satisfactorily in the Chevrolet 1½-ton truck shall meet also the requirements of the General Motors specifications for passenger-car hypoid lubricants. However, such a lubricant, of course, must be branded properly so that its use will be restricted to the heavy-duty truck.

Until more complete data are available from the field on the performance of the different types of hypoid lubricants in the heavy-duty-truck axle under actual service conditions in the hands of operators, separate specifications will not be issued by the General Motors Corporation on "truck-duty hypoid lubricants." The selection of lubricants for initial factory filling will be based largely on performance in the axle dynamometer test described under "tests on passenger-car and truck hypoid lubricants, herein." When and if it becomes necessary to issue separate truck hypoid-lubricant specifications, these specifications, like the present passenger-car hypoid-lubricant specifications, will be based on axle performance under service conditions; and the detailed physical and chemical requirements will be given only for the convenience of the manufacturing divisions in purchasing lubricants for initial servicing.

TESTS ON PASSENGER-CAR AND TRUCK HYPOID LUBRICANTS

A number of hypoid lubricants have been evaluated, for passenger-car and truck service, by our research laboratories in cooperation with the several car divisions of General Motors Corporation. The analytical data on these lubricants are given in Table 1.

These lubricants were evaluated for passenger-car duty in Chevrolet 1939 passenger cars, on the road, under the test procedure outlined in Table 2. This test generally is referred to as the "Chevrolet or proving-ground axle test," and is the performance test specified in Par. 2 of the General Motors specifications (July, 1939) for passenger-car hypoid lubricants.

These lubricants were evaluated also for truck duty in a Chevrolet 1½-ton truck hypoid axle, in the laboratory, on the rear-axle dynamometer shown in Figure 1. Torque equivalent to full engine torque in low gear is applied by the large direct-current dynamometer connected to the rear-axle propeller shaft. The output is absorbed by the two alternating-current dynamometers attached direct to the wheel shafts. These a.c. dynamometers may be controlled at different speeds so as to provide any desired degree of differential action; or may be synchronized, as in these lubricant tests, to eliminate differential action and allow equal power absorption through

TABLE 1

Composition of Lubricants Used in Axle Tests

Lubricant	Lead Soap Calculated as Lead Oxide	Total Saponifiable	Total Sulfur	Total Chlorine	Saybolt Viscosity at 210 Deg. F.
A	1.86	*	4.19	nil	83
B	1.31	25.78	1.69	1.10	113
C	nil	nil	1.20	3.20	81
D	nil	nil	1.60	2.80	80
E	nil	nil	0.12	2.79	68
F	nil	11.4	1.42	nil	91
G	nil	46.5	5.26	nil	84

* Present in lead soap.

both wheel shafts. The test conditions on the truck-axle dynamometer tests are outlined in Table 3.

A "passenger-car-duty hypoid lubricant," for use in General Motors passenger-car hypoid and highly-stressed spiral-bevel rear axles, is required to lubricate satisfactorily a current model Chevrolet passenger-car hypoid axle without scoring or scuffing when tested under the procedure given in Table 2.

Complete correlation between the truck-axle dynamometer test and performance in service is lacking. However, the best available data appear to indicate that a lubricant which will operate for a minimum of 500,000 cycles under the conditions (outlined in Table 3) without scoring or scuffing of the pinion or ring-gear tooth surfaces or corrosion of the bearings or machined surfaces, will function satisfactorily in the Chevrolet 1½-ton truck under field service conditions.

Axle tests, on the lubricants given in Table 1, made in both passenger-car and truck axles under the conditions outlined in Tables 2 and 3, are reported in Table 4.

Tests were made also on the Almen,[10] four-ball,[1] and SAE[6] extreme-pressure-lubricant testing machines for load-carrying characteristics. These machines, when operated under their respective standard testing conditions, separate the hypoid lubricants from the mild EP lubricants and straight mineral gear oils, but do not differentiate clearly between passenger-car and truck-duty hypoid lubricants. When more complete data are available on the performance of a larger number of hypoid lubricants in heavy-duty truck service, modified operating conditions may be developed for one or more of these laboratory testing machines—which, in conjunction with the chemical composition of the lubricant, will classify more accurately hypoid lubricants for use in the several makes and models of hypoid axles.

TABLE 2
Passenger-Car Hypoid-Axle Test

Sect. 1
- (a) Thoroughly clean axle housing and axle shafts, and install new third member.
- (b) Fill housing to the proper level with the lubricant to be tested.
- (c) Drive 3.8 miles at 60 m.p.h.
- (d) Drive 3.8 miles at 70 m.p.h.
- (e) Check axle for noise on a level concrete pavement, on the drive and coast, at 10 to 40 m.p.h. and 40 to 10 m.p.h. in high gear.
- (f) Drive 3.8 miles at 75 m.p.h.
- (g) Check noise as in item (e).
- (h) Drain lubricant into a clean container. Remove axle-housing cover and inspect the gears.

Sect. 2
- (i) If the gears have not scored under the high-speed driving conditions outlined in Sect. 1, replace the axle-housing cover and refill with the lubricant, which was drained in accord with item (h).
- (j) Drive car in high gear to 70 m.p.h. Disengage clutch and turn off ignition. Permit car to coast to 65 m.p.h., and immediately engage clutch as rapidly as possible with transmission in high gear and with ignition turned off. With clutch still engaged and ignition off, permit car to decelerate to 40 m.p.h.
- (k) Repeat item (j) six additional times.
- (l) Check noise, as in item (e).
- (m) Repeat item (j) eight additional times, making a total of 15 decelerations in high gear.
- (n) Check noise, as in item (e).
- (o) Drive car in second gear to 50 m.p.h. Disengage clutch and turn off ignition. Permit car to coast to 45 m.p.h., and immediately engage clutch as rapidly as possible, with transmission in second gear and with ignition turned off. With clutch still engaged and ignition off, permit car to decelerate to 20 m.p.h.
- (p) Repeat item (o) four additional times.
- (q) Check noise, as in item (e).
- (r) Repeat item (l) five additional times, making a total of 10 decelerations in second gear.
- (s) Check noise as in item (e).
- (t) Remove third member and inspect gears.
- (u) If the gears show no indication of scoring or scuffing on inspection [item (t)], a second third member is installed and the axle refilled with fresh lubricant, and the entire test is repeated.

Examination of the gears may be made at any time during the test procedure, if the axle becomes objectionably noisy, or if scoring or scuffing is suspected.

PASSENGER-CAR AND TRUCK HYPOID-GEAR LUBRICATION REQUIREMENTS

Engineering tests,[10, 11] and experience in service over a period of years, clearly indicate that active sulfur is required to prevent scoring or scuffing—under the most severe driving conditions at high speed—in passenger-car hypoid-gear axles. These conclusions are confirmed by the data reported in Table 4.

Dynamometer tests and a limited experience on the road indicate that the more-active sulfur compounds, that offer the maximum factor of safety in passenger-car axles at high speed, actually cause scoring, at low speed under high-torque conditions, in heavy-duty-truck service.

A complete understanding of the function of each of the several load-carrying addition agents under all conditions of speed and load is lacking. However, it is known definitely that, at high speed, passenger-car hypoid gears require the type of powerful extreme-pressure lubricants that function through the formation of solid films,[5, 9, 10] which act as "anti-welding" fluxes to prevent metal-to-metal contact between the sliding or rubbing surfaces. The sulfide films, which give adequate protection at high speed in passenger-car service, increase friction[5, 10]; and under the pressure-velocity (PV) conditions existing in truck service, at low speed and high torque, probably reduce the hardness or temper of the tooth surfaces sufficiently to permit scoring or scuffing. Under the truck operating conditions, the chlorine compounds appear to reduce friction. However, sulfur compounds—in which the sulfur more firmly is combined than in the very powerful passenger-car lubricants—still are required to furnish the necessary load-carrying properties.

TABLE 3
Truck Hypoid-Axle Dynamometer Test

Axle	Chevrolet 1½-ton
Axle ratio	6/37
Input torque	1,157 lb. ft.
Propeller-shaft speed	324 r.p.m.
Equivalent transmission gear reduction	7.227:1
Wheel-shaft speed	52.5 r.p.m.
Equivalent road speed (32 x 6 tire)	5.3 m.p.h.
Equivalent engine speed	2,342 r.p.m

These diametrically-opposed requirements necessitate a careful balance between "anti-weld" and "anti-friction" properties, and explain the difficulties in compounding a single lubricant that will meet the most extreme conditions in both passenger-car and truck service.

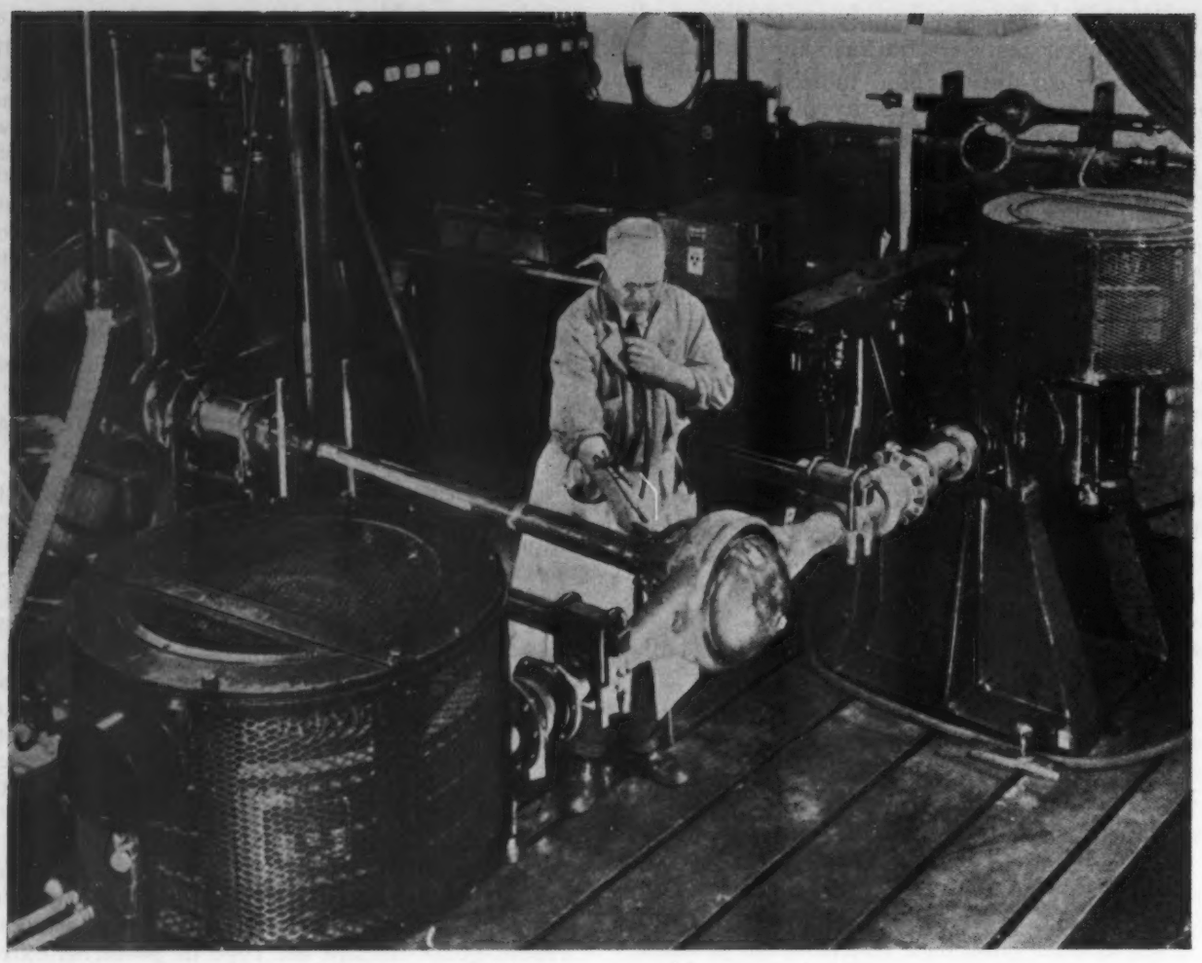

FIGURE 1
Rear-Axle Dynamometer.

COPPER-STRIP TEST

The copper-strip test and a wear test made on the Almen extreme-pressure lubricant-testing machine by determining the combined loss in weight of the pin and split bushings on operating 20 minutes under 8-pound load (4 weights on loading beam) have been proposed by one of the automotive manufacturers[7] for identifying the so-called active and non-active hypoid lubricants. The copper-strip and Almen-8-pound wear data, on the lubricants used in the axle tests, are given in Table 5.

TABLE 4
Axle Tests

Lubricant[1]	Chevrolet Passenger-Car Hypoid Axle Tested on Road in Accordance with Conditions Outlined in Table 2	Chevrolet 1½-Ton-Truck Hypoid Axle Tested on Dynamometer in Accordance with Conditions Outlined in Table 3
A	OK	Scored
B	OK	OK
C	OK	OK
D	OK	OK
E	Scored	Scored, Corroded
F	Scored	Scored
G	Slight Score	No Test

[1] The conditions (Table 3), under which the truck hypoid lubricants were tested, were originally designed for determining the fatigue life of the pinion gear teeth and may, as indicated in the text, be too severe for determining the scoring tendencies of a lubricant under service conditions.
Experience in the field may indicate that scoring tests must be conducted at a lower torque input, and that some lubricants that permit scoring under the high torque conditions outlined in Table 3 may be satisfactory in service.

Lead-soap active-sulfur hypoid lubricants and sulfurized mineral oils blacken copper at room temperature. Lubricants in which the sulfur more firmly is combined chemically do not blacken copper at room temperature, but may darken or blacken copper at 210 or 300° F. The minimum temperature at which darkening occurs, and the extent of the darkening, indicate roughly the degree of chemical combination or the activity of the sulfur. This test, however, may be quite misleading. The lubricant may contain a small amount of sulfur in a very active form, and may blacken the copper strip at room temperature, whereas the bulk of the sulfur in the lubricant may be combined too firmly to impart extreme-pressure characteristics.

Active chlorine does not appreciably affect the

TABLE 5

Lubricant	COPPER-STRIP TEST			Almen 8-Lb. Wear Test: Total Loss, Pins and Bushings, (Grams)
	5 Min. at 75 Deg. F.	1 Hour at 210 Deg. F.	1 Hour at 300 Deg. F.	
A	Positive	Positive	Positive	0.031
B	Negative	Negative	Tarnished	0.001
C	Negative	Negative	Positive	0.002
D	Negative	Negative	Positive	0.004
E	Negative	Negative	Negative	0.003
F	Negative	Negative	Tarnished	0.002
G	Negative	Tarnished	Positive	0.002

appearance of the copper strip. Sulfur and chlorine compounds, depending upon their activity, and on the amount present in the lubricant, in the absence of lead soap or some other suitable inhibitor, may corrode steel—particularly in the presence of water. Consequently, a positive copper-strip test indicates only the availability of a portion of the sulfur addition, and does not predict the behavior of the lubricant in service with respect to corrosion.[9, 10]

The Almen 8-pound wear-test data reported in Table 5, as well as a large number of tests made on mixtures of so-called active and inactive lubricants, indicate that this test may be considered only as a refinement of the copper-strip test—a quantitative copper-strip test—for more accurately evaluating the activity of the sulfur addition. A high Almen wear test, in the absence of foreign abrasive matter, generally indicates active sulfur. A high Almen wear test, therefore, may indicate that the lubricant is unsuited for truck service. However, a low Almen wear test does not necessarily indicate suitability for truck service—the lubricant may be low in load-carrying properties. Conversely, a high Almen wear test may indicate suitability for passenger-car service, but a low Almen wear test would not indicate necessarily that a lubricant is either superior or inferior for passenger-car hypoid gears.

GENERAL MOTORS RECOMMENDATIONS

Car-owner's instruction books and shop manuals specify the use of "passenger-car-duty hypoid lubricants" in all 1940 General Motors passenger-car rear axles and in the Chevrolet ½- and ¾-ton truck hypoid axles. "Truck-duty hypoid lubricants" are specified for use in the Chevrolet 1½-ton truck hypoid axle.

In order to meet the lubrication requirements of General Motors hypoid-gear rear axles "passenger-car hypoid lubricants" must comply with the requirements outlined in Par. 1 and 2 of the "General Motors Specifications for Hypoid-Gear Lubricants" (July, 1939), and "truck-duty hypoid lubricants" must be capable of operating a minimum of 500,000 cycles without scoring or scuffing of the gear-tooth surface under the conditions outlined in Table 3.

FUTURE DEVELOPMENTS

In converting from the spiral-bevel gear to the hypoid gear, most manufacturers took advantage of the higher tooth strength of the hypoid design, and reduced the diameter of the hypoid ring gear; but, as in the case of all new designs, full advantage of this increase in tooth strength was not realized, and the hypoid-gear set was not reduced to the minimum size or weight. An increase in speed and a further reduction in ring-gear size have been announced for 1940 production by at least one automotive manufacturer.

This trend toward the more efficient utilization of gear materials undoubtedly will be seen in many future axle designs. It, therefore, would appear that the lubrication requirements for hypoid-gear axles may become more critical, and that new types of extreme-pressure addition agents may have to be developed to meet future requirements.

The immediate problem is one of recognizing the difference in passenger-car and truck requirements, and of marketing to the car owner and car dealer the correct lubricant for each type of service.

BIBLIOGRAPHY

[1] H. Blok, "'Seizure-Delay' Method for Determining the Seizure Protection of EP Lubricants," *SAE J.* **44** [5] 193 (1939).

[2] Joseph Geschelin, "Lubrication of Special-Running Gear Mechanism," paper presented at SAE summer meeting, June 1938; excerpts, *SAE J.* **43** [3] 365 (1938).

[3] W. R. Griswold, "Hypoid Rear-Axle Design and Lubrication," *SAE J.* **40** [5] 194 (1937); *Proc. API* **17M** [III] 9 (1936).

[4] C. M. Larson, "Need for Simplifying Recommendations of Transmission and Rear-Axle Lubricants," paper presented at SAE summer meeting, May, 1937; digest, *SAE J.* **41** [3] 40 (1937).

[5] H. C. Mougey, "Commercial Situation of Automotive Extreme-Pressure Lubricants," *Proc. API* **15** [III] 60 (1934).

[6] *Soc. Automotive Eng. Extreme-Pressure Research Committee,* report by special subcommittee for correlating extreme-pressure-lubricant cooperative test-program data, presented at White Sulphur Springs, W. Va., meeting, June 1 (1936).

[7] E. W. Upham, Chrysler Corp., private communication to the author.

[8] W. A. Witham, "Hypoid Gears, Axles, and Lubricants," *SAE J.* **41** [5] 509 (1937).

[9] H. R. Wolf, "The Lubrication Requirements of Automotive Rear Axles," *Proc. API* **17** [III] 30 (1936).

[10] H. R. Wolf and H. C. Mougey, "Extreme-Pressure Lubricants—Correlation of Service Data with Laboratory Testing Methods," *Proc. API* **13** [III] 118 (1932).

[11] C. E. Zwahl, "Hypoid Lubricants—Test Results and their Interpretation," *SAE J.* **41** [6] 555 (1937).

Petroleum-ization–1940

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IN Petroleum-ization—1940, the numerous new processes for manufacture of high-octane gasoline, which have been filling the periodicals and the conversation of petroleum technologists during the past year or so, are discussed in plain language. Dehydrogenation, alkylation, isomerization, etc., are defined and described in a manner felt to be pertinent to the present potential applications of these processes to petroleum. In addition, in chart form and discussion, comparisons are presented to assist in locating, in the refinery picture, where these processes have application, and which should be considered for various refinery situations. The paper is an attempt to assist the organization and rationalization of the thoughts of refiners who may be viewing these developments with some alarm, and in some cases with considerable bewilderment.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

THE textbook of organic chemistry which has rubbed shoulders for so long with the piping handbook and the instrument catalogue on the bookshelf of the refinery office shows fresh thumb prints. The chapter on polymerization and the definition of a catalyst were reread carefully two years ago. Last year the index was leafed in vain in an effort to locate "hydrocodimer"! And now, smudges are in evidence on the hitherto-clean pages dealing with isomerization, alkylation, cyclization, and aromatization. The refiner, who for half a century has been handling one of the most complex mixtures of organic chemicals known to man, at last is talking organic chemistry—or, at least, he is in there trying! Although he does not know how to make it, he has found out that neohexane is 2,2-dimethylbutane, having astounding anti-knock value. Should he equip to manufacture neohexane, should he put in an alkylate plant, would it be the best bet to try catalytic cracking, or should he forget all about the whole business until somebody straightens out the tangle?

It is the purpose of this paper to attempt, in as plain language as possible, to place these various new processes on the checkerboard of petroleum refining, and determine which ones are competitive, which are complementary, and which should be considered for use as various refinery situations arise. However, due to the extremely-undeveloped state of some of these processes, a certain amount of forecasting based on personal opinion is woven into the pattern presented here, but it is hoped that this simplification and rationalization will assist the thinking which is necessary for the analysis and comparison of information which will be made available as time goes on. Discussion of the details of the operation of all of these various processes is beyond the scope of this paper; and, further, no comparison will be drawn between commercially competitive processes directed toward the same result.

DEFINITIONS AND DESCRIPTIONS

A certain number of definitions and descriptions will be useful in our study of the situation; and if these definitions do not agree exactly with the organic textbook, it should be remembered that they have been drafted for "petroleum-ization" rather than for the broad field of general organic chemistry.

Catalyst

A catalyst can be defined as a substance which, although present during a chemical reaction, apparently does not enter into the reaction but causes, by its presence, a change in the conditions under which that reaction occurs. Thus catalytic reactions offer a possibility for product control by selective acceleration of certain reactions which, in the opinion of many, is the most important phase of this new refining technique.

Hydrogenation

The hydrogenation process adds hydrogen to the hydrocarbon molecule. Hydrogenation may be either non-destructive or destructive. In the former, hydrogen is added to the molecule only if, and where, unsaturation with respect to hydrogen exists; thus the boiling range of the product is substantially the same as that of the charge to the process. In the latter, operations are carried out under conditions which result in rupture of some of the hydrocarbon chains (cracking); the hydrogen adding on, in general, where the chain breaks have occurred. A change in boiling range results from this type of hydrogenation, the degree of change depending on the operating conditions. Non-destructive hydrogenation is generally a low-temperature low-pressure operation, whereas destructive hydrogenation operates at high temperature and high pressure. Catalysts are employed in almost all hydrogenation processes.

Dehydrogenation

The general use of this term is so broad that it is practically useless. For example, the cracking of gas oil in an early Burton still involved dehydrogenation. For the purpose of this discussion, the term will be limited to operations on material in the gasoline boiling range, or lighter, and considered in two categories, as was done for hydrogenation, i. e., non-destructive and destructive. Non-destructive dehydrogenation is defined as the removal of hydrogen from the hydrocarbon molecule without the cracking which would change significantly its boiling range. Destructive dehydrogenation removes hydrogen from the molecule, but is accompanied by chain

rupture to some degree. Catalysts are employed for the non-destructive dehydrogenation, but the destructive dehydrogenation may be carried out either with or without catalysts—depending on the degree of selectivity desired.

Polymerization

Broadly speaking, polymerization can be considered as the linking of two or more hydrocarbon molecules to form one molecule having a longer carbon chain and a higher boiling point. Here again the definition must be narrowed to make it useful, because the tar produced when gas oil is cracked in a conventional cracking coil is the result of polymerization. Polymerization, as practiced intentionally, at the present time is confined to hydrocarbons having four carbon atoms or less to the molecule (butane and lighter), and links them together under conditions which result in the product being predominantly within the gasoline boiling range. The operation can be carried out either catalytically or thermally. The catalytic process operates at relatively high pressures, but at moderate temperatures, and only the unsaturates in the charge react. The thermal process operates at high pressures and high temperatures, but reacts both unsaturates and saturates—due in part, but not entirely, to thermal dehydrogenation taking place in the heating coil as the charge is brought to operating temperature.

Alkylation

If any saturated hydrocarbon molecule is deprived of a hydrogen atom and then united with another hydrocarbon molecule through the bond where the hydrogen atom was removed, alkylation has been accomplished. The broad definition of this term leaves us nowhere, but one of the specific alkalytion processes in which interest is at a high pitch at the present time unites *iso*butane (a branched-chain compound) with a butene (unsaturated branched- or straight-chain compound) to produce practically pure *iso*octane. The operation is carried out at low pressure and low temperature, and requires a catalyst. Another example is the process which produces neohexane. In this process ethylene is reacted with *iso*butane to produce a saturated highly-branched-chain six-carbon-atom compound. The neohexane process uses no catalyst.

Desulfurization

In the broad sense, this term is self-defining, but here it will be considered as applying to the removal of sulfur from material within the gasoline boiling range. Chemical desulfurization, using either sulfuric acid or caustic soda, has been practiced for many years; and it should be mentioned, in passing, that strict economic comparisons must be made—the old versus the new—before completely revamping the refinery. There is, however, a definite feeling that chemical desulfurization is on the way out; so, for the purpose of this summary—which is concerned chiefly with the new catalytic processes—the definition will be narrowed to identify processes which decompose the sulfur-hydrocarbon compounds in the gasoline, and evolve the sulfur as hydrogen sulfide or possibly as sulfur dioxide. Desulfurization and dehydrogenation tend to proceed hand in hand, but the interest which is aroused at present is due to knowledge which has permitted the control of the relative rates of these two types of reactions by the use of catalysts. The now proven deleterious effect of sulfur compounds in gasoline on octane number and lead susceptibility has given a dollar impetus to further advances in desulfurization methods for sulfur removal alone. This is a distinct contrast of previous trends of thought, in which the sulfur reduction which accompanied various forms of dehydrogenation was accepted for what it was worth in meeting sulfur specifications of the gasoline—without giving too much thought to control and selectivity.

Isomerization

Inasmuch as saturated hydrocarbons can exist as either straight- or branched-chain compounds, and as the branched-chain compounds in the gasoline boiling range have higher anti-knock qualities than the straight-chain compounds (e. g., *iso*octane vs. normal heptane, the 100 and 0, respectively, of our anti-knock scale) interest in controlled changing of straight chains to branched chains (isomerization) will increase sharply if practicable methods can be discovered. Isomerization, as now available for our study as an isolated process, is confined to butane and pentane conversion to the corresponding *iso*compounds; but inasmuch as the extremely high octane-number increase obtained during certain catalytic-dehydrogenation operations on gasoline best can be accounted for by assuming some isomerization to have occurred, it is the opinion in many quarters that catalysts and conditions will be found eventually which will extend isomerization as a controlled process into the broad gasoline boiling range.

Aromatization

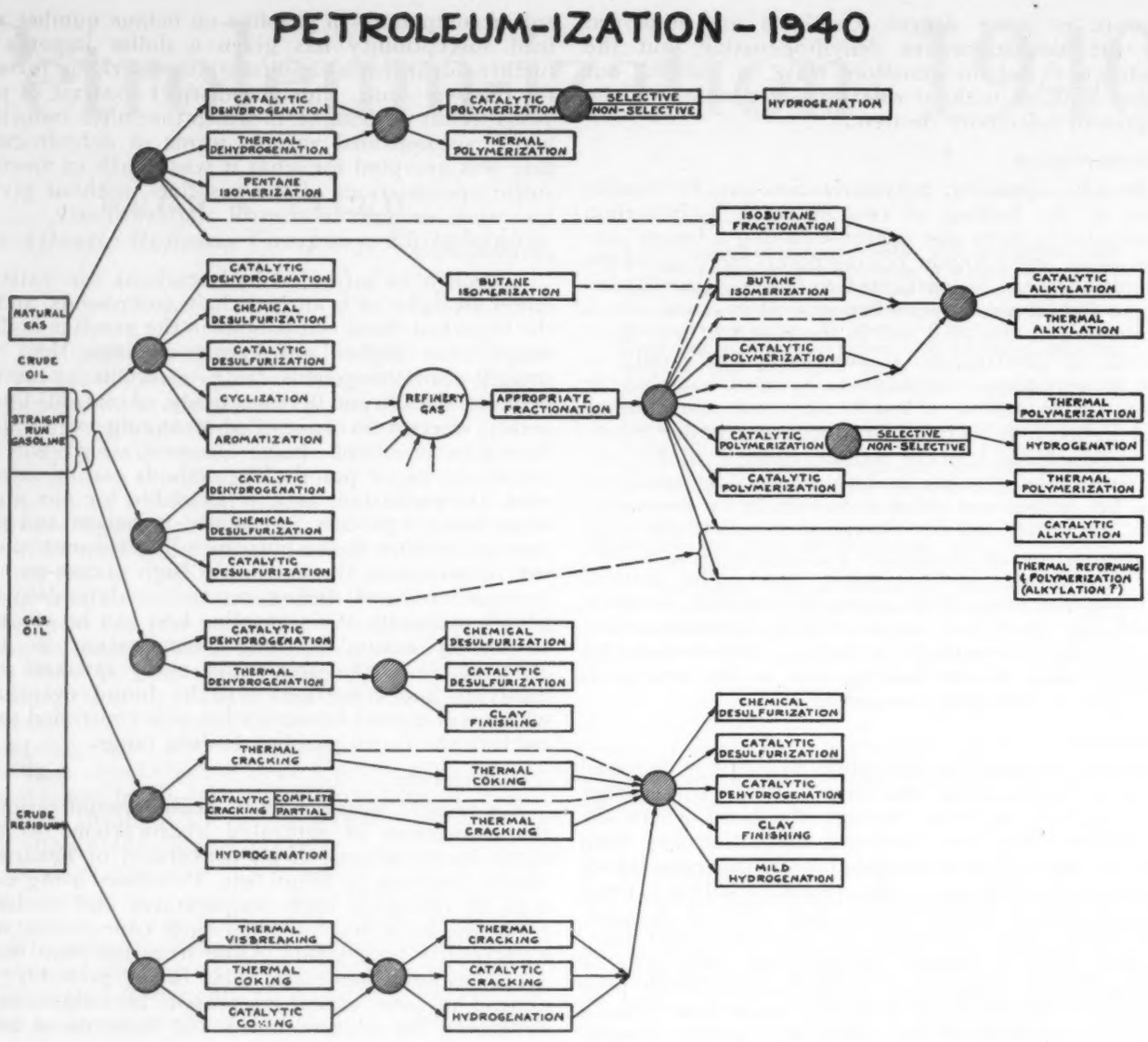
For present purposes let us define aromatization as the conversion of saturated hydrocarbons to aromatic hydrocarbons, e. g., conversion of hexane to benzol, heptane to toluol, etc. Processes using catalysts at relatively high temperatures and moderate pressures have accomplished such conversions with surprisingly high yields. Aside from the "war-baby" aspect of such processes, their future probably will depend to some extent on present investigations to determine the relative merits and demerits of inclusion of aromatics in fuel for use in high-power aviation engines operating at high altitudes.

Cyclization

This process is the conversion of straight-chain hydrocarbons to ring compounds (cyclics) but without the attendant dehydrogenation which necessarily takes place during the production of aromatics. The development of cyclization as a definitive process is tied in with the remarks previously made about the future of aromatization. The process doubtless will be catalytic, but it is still over the horizon, and cannot enter too seriously into present thinking.

Catalytic Cracking and Reforming

As mentioned previously, cracking involves dehydrogenation of the type defined as destructive. In the rupturing of the hydrocarbon chains, there are created fragments which are extremely active chemically. In the course of reacting to attain chemical stability, these fragments apparently, to some degree, engage in practically all of the reactions which we have been discussing. The use of a catalyst during cracking has the interesting effect of decreasing the amount of polymerization to tar and at the same time encouraging aromatization and isomerization of the cracked fractions in the gasoline boiling range. As a result, material of high anti-knock value is produced. In catalytic reforming a different effect is sought.



Here aromatization and isomerization are encouraged by different operating conditions and catalysts, but every effort is made to suppress the chain rupture which would cause excessive conversion of gasoline to gas. In the following discussion, catalytic reforming is classified as dehydrogenation, but merely for convenience, and does not infer that the dehydrogenation phase is considered predominant.

Coking

The operation of coking, whether thermal or catalytic, consists of heat-treating heavy hydrocarbons, usually crude residuum or cracked tar, in order to increase the ultimate yield of gasoline from the crude. Heavy hydrocarbons are low in hydrogen-carbon ratio; gasoline is relatively high in this same ratio. The conversion, therefore, necessitates the throwing out of carbon (coke) as a means of adjustment of this ratio. Catalytic coking, as contrasted with thermal coking, results in less coke "throwout" for a given conversion, possibly due to the fact that gasolines of relatively high aromatic content have a lower hydrogen-carbon ratio than non-aromatic gasolines, and lower carbon "throwout" would suffice for the adjustment in hydrogen-carbon ratio necessitated by this type of conversion. It is important to note that the carbon produced in the catalytic operation deposits in the pores of the catalyst; therefore, extensive steam generators must be included as a part of the plant investment if the heating value of the carbon is to be put to use when the catalyst is regenerated.

REFINERY APPLICATIONS

Having had a general look at these new processes, the refinery picture should be examined for possible applications. For this purpose a chart has been prepared, which starts with crude petroleum and presents some of the various courses which might be plotted in converting this crude to gasoline as the major product. The shaded circles are positions where a stop is made to review ways and means, before taking the next step.

NATURAL GAS

The natural gas, butane and lighter (except when pentane isomerization is indicated) can be converted to either high-octane motor gasoline or to aviation gasoline. Because natural gas is, in general, completely saturated, either catalytic or thermal dehydrogenation is necessary. If motor gasoline is the goal, this choice is governed by investment and operating-cost estimates. If aviation gasoline is desired, or if flexi-

bility for future changes to aviation production is a requirement, the choice probably will be catalytic.

Essentially the same reasoning applies to choice of type of polymerization unit. If aviation gasoline is not desired, the investment comparison must take cognizance of the fact that the dehydrogenation is an integral part of the thermal-polymerization plant.

If a catalytic-polymerization plant is chosen, the decision must be made between selective operation for codimer (*iso*octene) followed by hydrogenation to hydrocodimer (*iso*octane) or non-selective operation for a higher yield of high-octane (80+) motor fuel. Perhaps a plant built for selective operation, but operated for motor fuel and without hydrogenation, is indicated in order to avoid closing the door to future aviation-gasoline production from this stream.

If hydrocodimer is produced, a high-octane front-end volatility correctant can be prepared by isomerizing some of the normal pentanes in the crude to *iso*pentane. This step is indicated if the loss in octane rating of the hydrocodimer when blended with natural gasoline is sufficient to justify the investment and operation of such a plant.

The indicated approach to *iso*butane fractionation or butane isomerization will be discussed in connection with handling refinery gas.

STRAIGHT-RUN GASOLINE

The light fraction of the straight-run gasoline may be subjected to catalytic dehydrogenation (catalytic reforming) for the purpose of making a high-octane (85+) aviation fuel with good lead susceptibility. If the octane-number increase does not justify the sacrifice in yield which accompanies the reforming, catalytic desulfurization alone may be indicated to produce low-sulfur stocks for special naphthas or to take advantage of the increase in lead susceptibility which results from the sulfur removal alone. As previously mentioned, this latter step must stand the careful economic scrutiny of comparison to chemical treatment.

Cyclization to increase anti-knock value without conversion to unsaturates or aromatics may be a profitable possibility in the future.

Aromatization will produce aromatics which may have value as a component of the aviation fuel of the future. If the process can be developed to a position competitive with other methods of anti-knock increase from a cost standpoint and material degradation, a wide application will be made, inasmuch as the motor-fuel blending stock produced has a much higher octane value when measured on the road or chassis dynamometer than when measured by the ASTM motor method.

The entire straight-run gasoline can be dehydrogenated catalytically or desulfurized, with the choice developed using the same reasoning that was used for the light fraction. The straight-run gasoline available also should be kept in mind when laying plans for processing the refinery gas, as will be seen later.

The heavy straight-run gasoline, long the standard charge for thermal reforming, can be dehydrogenated catalytically to produce a high yield of high-octane desulfurized blending stock. However, it should be remembered in planning this operation that the change in boiling range is much less with catalytic than with thermal dehydrogenation. If thermal reforming has been used to control overall gasoline volatility for the refinery, care must be taken, or the entire plant-volatility balance may be upset by this loss of front-end volatility. If this develops to be serious, this fraction may be left for thermal reforming; but, inasmuch as the desulfurization obtained is less than half that which would have been experienced by using the catalytic unit, catalytic desulfurization of the thermally-reformed naphtha may be justified. As a last possibility, if the sulfur situation is not serious and the catalytic desulfurization cannot be justified, the good old standbys, vapor-phase clay treatment or chemical treatment, may be used.

GAS OIL

The gas-oil fraction from the crude may be charged to the existing thermal-cracking units. This is a cheap way to make gasoline from gas oil; and, inasmuch as we still are learning more every day about how to operate thermal-cracking coils, let us not be too hasty in discarding these reliable units. Some discarding may be necessary, but we must be certain that the change is an improvement, and not just a change.

If the refinery is situated so that heavy fuel oil is difficult to market, thermal coking may be indicated on the cracked tar; but the refractory gas oil obtained from this type of coking generally is conceded to be a poor cracking stock. A careful economic analysis is necessary to make the decision, and this analysis should be repeated at intervals as refinery markets change to determine the advisability of continuing the operation.

If analysis indicates that some or all of the gas oil should be cracked catalytically to produce high-octane (76+) gasoline, a decision must be made as to whether the operation will be partial (once-through) or complete (recycled to ultimate gasoline yield). The type of process and the stock to be handled must be examined critically in order to reach a decision on this point. If a once-through operation is practiced, the catalytic recycle can be handled in thermal-cracking coils (possibly existing) for completion of the conversion. If a furnace-oil market exists that can absorb this catalytic recycle, the situation is improved—inasmuch as the opinion persists that the recycle gas oil from a catalytic cracking unit is not the easiest thing to handle from a cost standpoint for further processing either catalytically or thermally.

The gas oil may be considered as a possible charge for a destructive-hydrogenation unit; but information at present indicates that, unless specialty products are desired, the low octane value of the gasoline, plus the high investment and manufacturing costs, is not offset by the high ultimate yield and the high quality of the gasoline in respects other than octane value. Present product-price structures do not favor hydrogenation at this point.

CRUDE RESIDUUM

The crude residuum or natural tar may be charged either to a thermal viscosity breaker to obtain maximum gasoline without running to coke, to a thermal coking unit to obtain a high ultimate gasoline yield, or to a catalytic-coking unit to obtain the highest yield which can be obtained without hydrogenation. If the catalytic unit is considered, possible duplication of steam-generating facilities must be evaluated. Although some gasoline is produced directly in these operations, the prime function in all is the production of gas oil for subsequent conversion to gasoline. This

gas oil is similar to the gas oil from the crude, and may be considered in the same category for purposes of simplification.

CRACKED GASOLINE

The finishing of cracked gasolines can take four possible major routes. If octane level is satisfactory, catalytic or chemical desulfurization may be indicated; but a word of caution is necessary here. Data from catalytic desulfurization of straight-run gasolines show extremely satisfactory results; but, in attempting to handle cracked gasolines in the same manner, some processes have had trouble obtaining the required degree of desulfurization without resorting to operating conditions which resulted in excessive yield loss by polymerization or dehydrogenation.

If the octane level is unsatisfactorily low on the cracked gasoline, catalytic dehydrogenation should be given consideration. Although thermal reforming seldom has been an economically-sound operation applied to cracked gasolines, there are definite indications that catalytic operations have possibilities in this respect.

Vapor-phase clay treatment, or chemical treatment, is the answer if neither sulfur nor octane value requires serious attention; but this phase of refining should not be passed without looking at hydrogenation. The possibilities in hydrogenation for sulfur removal, in the event the catalytic-desulfurization processes fall down on cracked gasolines, should not be overlooked. This hydrogenation would be mild in character, using catalysts which would function in low-cost low-pressure plants, and operating in such a manner as to remove sulfur selectively without seriously reducing the octane level.

REFINERY GAS

Most of the operations considered up to this point produce some gas in addition to liquid products. This gas can be a very profitable source of either aviation gasoline or motor fuel. The various steps that can be taken to realize profits from this situation are quite varied, particularly as much depends on the type of gas available which, in turn, is a function of crude run and previous processing methods. The best that can be done here is to discuss the possibilities and indicate the type of thinking necessary to evaluate a given situation.

If a catalytic-alkylation plant is being considered for production of aviation gasoline (96+ octane), three possible channels must be considered. These three considerations are necessitated by the requirement that the feed to the alkylate plant must contain *iso*butane and butenes in molecular ratio of slightly more than 1 to 1. Most refinery gases contain one-third to one-half the quantity of *iso*butane necessary to supply this requirement; and, if no steps are taken to correct the situation, the alkylate produced will be too low in octane rating.

The first possibility is fractionation of natural gas for its *iso*butane content and addition of this to the refinery gas in proper amounts to meet the requirements. This necessitates having available and handling large quantities of natural gas.

The second possibility is isomerization of butane to *iso*butane to a sufficient degree to build up the *iso*butane-butene ratio. In refineries having highly-unsaturated gas it may be necessary, in addition to this, to isomerize some of the butane from natural gas to augment the *iso*butane available.

The third possibility lies in the other direction, i. e., reduction of the content of butenes, by catalytically polymerizing some of these butenes. The butanes pass through this process unchanged; and although in a given refinery this method produces considerably less alkylate, it does produce, more or less as a by-product, high-octane polymer gasoline for use as a motor-fuel blending stock.

Both catalytic- and thermal-alkylation processes are shown on the chart. As previously mentioned, the eight-carbon-atom alkylate is made in a catalytic process now commercially available. The thermal-alkylation process previously mentioned which produces neohexane, a six-carbon-atom alkylate, is not as completely developed at present, but is sufficiently close in accomplishment to be considered competitive for this survey—particularly as the thermal alkylate is a superior product in anti-knock value (120+ vs. 96+).

If motor fuel is the goal in processing the refinery gas, polymerization should be considered; inasmuch as, at the present time, an alkylation plant is difficult, if not impossible, to justify economically for motor-fuel production.

Thermal-polymerization units have a high investment cost, but do produce high yields of high-octane (76+) gasoline. This high yield is due to the inherent dehydrogenation which takes place in the plant heating coils, plus a certain amount of alkylation which occurs between the saturates and unsaturates. In addition to the octane credit, the thermal polymer should be given a high volatility credit. Thermal polymer gasoline is extremely rich in front-end volatility; and, properly evaluated, this credit may amount to more than the octane credit.

Catalytic polymerization, if operated selectively and in conjunction with a hydrogenation unit, is directly competitive with the alkylation process in producing *iso*octane. In this comparison of processes, the possible necessity for isomerization of butane for the alkylation plant must be considered and compared with the probable necessity for isomerization of pentane as a blending stock for the hydrocodimer. Alkylate has inherently better front-end volatility characteristics than hydrocodimer, which may give the alkylation process an economic advantage in certain circumstances.

If a non-selective catalytic-polymerization plant is being considered, the competition is with the thermal unit—both being considered for motor-fuel production. Inasmuch as the catalytic unit reacts only the unsaturates, the ultimate gasoline yield from a given gas stream is considerably lower. However, the investment and operating costs are substantially lower, and units much smaller in capacity than would be practicable for a thermal unit can be considered. The catalytic-polymerization unit is definitely a "cream skinner," with a quick payoff and, as such, should be examined carefully, particularly for a small refinery.

In a large refinery the application for catalytic polymerization well may be in conjunction with a thermal unit, utilizing the "skimming" effect cheaply to polymerize the unsaturates—the thermal unit following to complete the cleanup. Further, excess or standby capacity for peak or abnormal loads can be installed and operated cheaper catalytically than thermally. For the large refinery this combination of catalytic and thermal polymerization is probably the most flexible setup that can be obtained commercially at the present time. This is particularly true if the

catalytic plant is designed for either selective or non-selective operation.

The possibility of catalytic dehydrogenation prior to catalytic polymerization has not been discussed in connection with refinery gas, but was mentioned for natural gas. Processing natural gas, particularly for aviation gasoline, seems to be the most promising place for application of this combination at the present time, due to the relatively high investment costs for butane-dehydrogenation equipment. If this situation changes in the future, and it is believed that it will, consideration should be given to refinery-gas applications for catalytic dehydrogenation.

The last two processes indicated handling refinery gas, and involve simultaneous processing of the straight-run gasoline from the crude. Thermal reforming and concurrent gas polymerization was developed initially in an effort to give the small refinery a chance to obtain the advantages of thermal polymerization by combining the operation with thermal reforming, in the same coil. Developments have shown that more than concurrent reforming and polymerization take place. Possibly both alkylation and isomerization play a role in the surprisingly satisfactory results obtained. The possibilities of such combined processing should not be neglected in studying a large refinery, particularly as rumor has it that a catalytic-alkylation process is in the offing which produces excellent results from such a combined charge.

CONCLUSION

In conclusion, it was the hope, in the preparation of this discussion, that if nothing else was accomplished one thing at least would make an impression. With these many and varied processing methods unfolding before our eyes, as research digs deeper into the chemical behavior of hydrocarbons, the future of petroleum refining takes a new form. There is a vision of no longer having to take what the crude has to offer, marketing the products for what they are worth; but rather the day is approaching when, as a result of knowledge acquired by exercising ingenuity, patience, and diligence, the end products of petroleum processing will have the desired chemical and physical properties, regardless of the type or nature of the crude oil entering the charging lines. The plant no longer merely will refine crude oil, but rather it will, by precise physical and chemical processes, transform crude oil. The past decade has seen tremendous changes in this respect; the next 10 years are unpredictable, but they promise to be fast-moving and interesting.

New Thermofor Kiln

Continued from page 66

the advantages of the Thermofor kiln outlined above result in large savings in expenses for fresh clay, clay handling, filter washing, filter blowing, solution distillation, wash-oil handling, clay burning, clay disposal, maintenance, oil losses, and oil degradation. These savings are magnified further in the case of many solvent-refined oils having good response to clays regenerated by carbonization. Economic calculations for three typical lubricating-oil refineries—one on 100 percent Pennsylvania crude, a second on Mid-Continent and Gulf Coastal crudes using both acid and solvent refining, and a third on Mid-Continent crude using almost 100 percent solvent refining—show that Thermofor kilns give very quick investment retirements. Conservative estimates show payouts of one to two years for equipment investment plus paid-up royalty; and, in cases in which running royalties are employed, payouts of less than a year are indicated.

Thermofor kilns are attractive for large- and small-scale installations. Two commercial units are now actually in operation, one having a capacity of 50 tons per day and another 10 tons per day. A third unit of 120-tons-per-day capacity is under construction, and will be placed in operation in the near future. The equipment investments for commercial units with necessary auxiliary feed hoppers and temperature-control devices, but exclusive of clay conveyors, will be 25 to 50 percent less than those for multiple-hearth installations handling the required amount of clay to give the same decolorizing capacity. Burners as low as 10-tons-per-day capacity can be built without any serious disadvantage in price due to smallness.

Another important advantage of the Thermofor kiln is that its installation automatically increases percolation-plant capacity by a substantial proportion. For example, in a typical refinery in which clay is regenerated and segregated 10 times and is discarded after the tenth cycle, the average clay efficiency for the entire plant is only 66 percent based on fresh clay. With a Thermofor kiln in operation and fresh clay being added only to make up for losses (2 percent per cycle assumed) the clay efficiency of the same plant can be maintained at an average of 95 percent. This increase in clay efficiency reduces the washing, loading, and unloading time on the filters by 30 percent of the normal requirement, and increases proportionately the time for percolation. In this particular case the gain in percolation time represents a 15-percent increase in the overall filter-plant capacity.

The API Hydrocarbon Research Project

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THE API hydrocarbon project was undertaken as the result of a rapidly-increasing need for basic data on the combustion characteristics of gasoline hydrocarbons to be used as guides in the solution of problems encountered in the development and utilization of internal-combustion-engine fuels. There also exists an acute demand for more complete and accurate physical and thermal data for many of the hydrocarbons in this range than now exist. Several excellent compilations of the latter type of data, plus knock ratings by conventional methods, are available. A scrutiny of these compilations, however, reveals a large number of blank spaces along with many items which, in the light of present knowledge, are either incomplete or of questionable accuracy. In particular, knock ratings by the conventional laboratory methods are unsatisfactory from a basic point of view, as it is recognized by all who intimately are concerned with this type of work that behavior under many conditions of utilization rarely can be predicted from such ratings. This is illustrated in Figure 1, which compares the knocking behaviors of 5 fuels under 12 different test conditions.

The project was undertaken as the direct result of the voicing of the above need (during an informal discussion following a CFR* meeting early in 1938) and a proposal by the Research Foundation of Ohio State University inviting support for a program aimed primarily at research upon methods of hydrocarbon preparation. As originally expressed, the two proposals represented quite divergent aims: the former involved the extensive examination of a large number of representative hydrocarbons (which necessarily would be required in rather large quantities in order to permit comprehensive engine studies); the latter to investigate methods of preparation—the question of quantity being quite unimportant. The objectives of the two programs were discussed quite thoroughly, with the result that Professor Boord of Ohio State University Department of Chemistry (who was interested primarily in the prepara-

* Cooperative Fuel Research Committee.

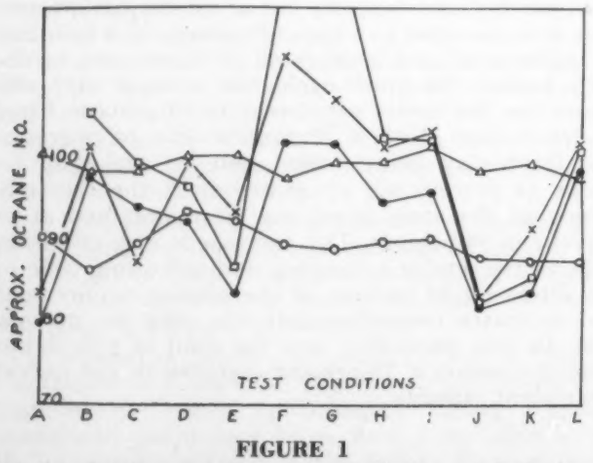

FIGURE 1
Variation in Apparent Knocking Behavior, of 5 Fuels of Widely-differing Composition, with 12 Test Conditions.

THE API hydrocarbon research project was initiated September 1, 1938, for the purpose of preparing as many gasoline-range hydrocarbons as possible and examining them for their basic engine-combustion characteristics, physical and thermal properties, etc. No extensive chemical studies are anticipated. The program is sponsored by 25 interested companies. The hydrocarbon preparation is being carried out by Prof. C. E. Boord of Ohio State University Research Foundation. Engine studies, which consist of conventional ASTM and CFR research ratings, plus the determination of permissible critical compression ratios under four widely-varying conditions of service, are being conducted by the Research Laboratories of the General Motors Corporation. Physical- and thermal-property determinations are to be conducted by individuals who are engaged in research upon the particular properties under consideration. To such investigators, the project will make available highly-purified hydrocarbons in reasonable quantities.

Up to the present, about 12 hydrocarbons, all in the 8-carbon-atom range, have been prepared and submitted for engine examination. In addition, a considerable number of hydrocarbons are in the process of examination, or have been completed, with the exception of final purification. It is anticipated that approximately 40 hydrocarbons will be prepared and examined during the present year. It was not possible to complete the work on very many hydrocarbons during the first year, as much of the time was utilized in organizing the staff of the hydrocarbon laboratory at Ohio State University and in working out the details of the engine-test procedure. The basic method used for engine studies consists in determining the critical compression ratios over a wide severity range, which includes conditions less severe than the CFR research method, to a set of conditions which has been demonstrated to be more severe than those ordinarily encountered in aircraft practice. No attempt is being made to centralize either the preparation or examination of work upon hydrocarbons of any particular characteristic or for any special type of service. The basic plan is to map the gasoline-range field as thoroughly as possible for the purpose of providing a background for any specialized development work which individual organizations may wish to undertake.

The present paper has been prepared primarily to outline the objectives of the project; and the method of attack and subsequent papers, to be given by individual investigators, will present experimental results.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

tion proposal) agreed to extend the scope of that project to provide quantities sufficient for engine research purposes. These discussions culminated in a meeting of the interested parties at Wichita, Kansas, at the time of the 1938 Institute's mid-year meeting. It was the vote of the group present that the work be undertaken, and that it be sponsored by the American Petroleum Institute. An application for such sponsorship subsequently was acted upon favorably by the directors of the American Petroleum Institute, the understanding being that the project would furnish its own funds.

As finally organized, for the first year the project had 25 supporting organizations. Work upon this project was begun officially on September 1, 1938, and the first year's activities terminated August 31, 1939. The project has been renewed for a second year beginning September 1, 1939, with 24 supporting organizations.

GENERAL PROGRAM

1. Organization and Administration

The general plans under which the work is being carried out were formulated at the initial meeting held in August, 1938. The basis for organizing the program was as follows:

1. As many hydrocarbons falling in the gasoline-volatility range will be prepared as experience should find possible and practical. These hydrocarbons should be available in sufficient quantity to permit the carrying out of a basic study of engine-knocking characteristics and a reasonably-complete examination of their physical and thermal properties. No restrictions will be placed upon the type of hydrocarbons to be prepared—it being understood thoroughly that the program is to be of a basic research nature, and not one of specific product development.

2. The hydrocarbons are to be subjected to the most basic possible study of their knocking characteristics.

3. Physical and thermal characteristics are to be determined both for purposes of identification, and to amplify the existing data upon these points.

4. No extensive studies of chemical characteristics are contemplated.

5. The results of all findings are to be made public. The committee further went on record: "While it is not anticipated that patentable developments will arise out of this project, it is understood that if such should arise, benefits will be dedicated to the public by publication or otherwise."

6. It was recommended that the Research Foundation of Ohio State University undertake to secure—and, when necessary, to prepare—hydrocarbons falling within the scope of the project.

7. The Research Laboratories of General Motors Corporation were requested to undertake the engine studies.

8. The determinations of physical and thermal properties are to be carried out by whatever procedure appears to be most expedient in individual cases.

The broad plan adopted at the first meeting of the Hydrocarbon Research Committee anticipated that the work probably would extend over a period of approximately four years. It was felt, however, that support should be given upon an annual basis, with the decision for each succeeding year's support contingent upon progress. It was not anticipated that all of the hydrocarbons falling in the gasoline range will be prepared and examined under the above-mentioned conditions, within the time indicated. This would be a physical impossibility, as is indicated by the tremendous number of hydrocarbons which are theoretically possible in the gasoline-volatility range. It was determined, however, that hydrocarbons broadly representative of the various types which possibly might be employed as internal-combustion-engine fuels would be investigated to the fullest possible extent.

The project currently is administered by a committee consisting of a representative of each organization supporting the project. This committee met upon three occasions during the first year of the program. One meeting was held in August, 1938, for the purpose of organizing and authorizing work and expenditures under the project. Meetings also were held at the time of the 1938 annual meeting and the 1939 mid-year meeting of the Institute. Another meeting of this committee will be held at the time of the 1939 annual meeting. Handling of detailed questions rests with a small advisory committee. A complete list of the project underwriters and their representatives is attached as Appendix 1 of this report.

2. Hydrocarbon Preparation and Procurement

As indicated hereinbefore, no attempt is being made to prepare or secure all of the hydrocarbons falling within the gasoline-volatility range. The hopelessness of such an ambition is indicated by the tabulation below, which shows the number of isomers possible in the C_5 to C_{12} range.

Accordingly, selection of the hydrocarbons to be prepared is being determined largely by practical considerations. In general, it is felt that the scope should be restricted to those hydrocarbons falling within the C_5 to C_{12} range, inclusive. In the first year's work particular emphasis was placed upon the preparation of the 8-carbon-atom paraffins. Hydrocarbon preparation was delegated to the Research Foundation of Ohio State University—with the understanding that a suitable personnel organization would be created, and that the necessary physical facilities would be acquired. All out-of-pocket expenses directly resulting from the prosecution of the project were to be borne by the supporters of the project. A suitable budget was prepared for the first year, and work was begun officially in September, 1938. The original Ohio State University proposal involved research into methods of preparation only with the idea that the quantities actually to be prepared would be quite small. The most frugal engine procedure which could be devised indicated that at least 1 gallon would be required. Accordingly, the methods of attack originally proposed by Ohio State University were revised, with the idea that *at least* 1¼ gallons of each hydrocarbon would be made available. The minimum of 1 gallon would be required for the basic engine studies, whereas 500 ml. of material of the highest possible degree of purity was to

Carbon Atoms	Insomers: Paraffins (C_nH_{2n+2})	Insomers: Olefins (C_nH_{2n})
5	3	5
6	5	13
7	9	27
8	18	66
9	35	153
10	75	377
11	159	914
12	355	2,281
	Hanze and Blair *J. Am. Chem. Soc.* **53,** 3077	Hanze and Blair *J. Am. Chem. Soc.* **55,** 680

be available for physical- and thermal-property examination.

3. Engine Studies

The carrying out of the engine research work was delegated to the Research Laboratories of the General Motors Corporation, particularly as this organization had contributed already a considerable portion of the available basic information bearing on the principal objective of the project. A thorough study was made of a possible means of attack, with the result that a series of four tests involving the determination of critical compression ratios under widely-varying severity conditions was recommended to the committee, and selected as the basic engine study. These tests are supported by ASTM and research octane numbers upon the hydrocarbons either direct or when blended with a 60-40-octane-heptane base (in the event that their initial octane numbers are above 70). These latter observations include additions of 1 ml. and 3 ml. of tetraethyl lead per gallon. The program also provides for studies at varying mixture ratios, when availability of the hydrocarbons will permit. It was agreed that this work would be amplified, whenever possible, by other engine studies such as supercharge tests. The initial work has included the examination of a series of easily-obtainable fuels representing a wide variation in type under a large number of test conditions. The net result of this work is to indicate the practicability of the method of approach that has been followed. It should be emphasized that an important consideration in setting the scope of the basic engine-test program is the limitation imposed by the quantities which can be prepared by practical procedures.

4. Physical and Thermal Properties

No definite plans have been drawn up for the conduct of physical- and thermal-property studies. It has been the feeling of the committee that such work best can be done by specialists in particular fields of research. Accordingly, it is the plan of the project to make the purified hydrocarbons available to competent research workers—the understanding being that the information obtained will be made available promptly to the committee, but that the individual worker will have the right to independent publication of his results. In addition, the project is cooperating with the National Bureau of Standards, which is engaged in a hydrocarbon research program of a more specialized nature under the sponsorship of the National Advisory Committee for Aeronautics.

HYDROCARBON PREPARATION

1. Personnel

The work of procuring those hydrocarbons already available from other sources, and preparing those otherwise unobtainable, was delegated to the Research Foundation of Ohio State University. A "hydrocarbon laboratory" has been established under the general supervision of C. E. Boord, professor of organic chemistry. A research staff has been established as follows:

A. L. Henne, research associate in charge.
1 research assistant.
3 graduate fellows (half time).

In addition, the services of another research assistant and three graduate fellows have been utilized for comparatively short periods. It is anticipated that this basic arrangement will be employed for the entire program. Whether it will be amplified at some later date will be determined by subsequent developments.

2. Preparation Procedures

Certain of the hydrocarbons falling within the scope of this project are obtainable without recourse to laboratory preparation. Accordingly, as many as possible have been procured and purified—whenever necessary—at Ohio State University. For example, the following is a partial list of the hydrocarbons obtained in this manner:

Benzene
Toluene
Ethyl benzene
*m*Xylene
*o*Xylene
Cyclohexane
Methylcyclohexane
3-hexene
2,2,4-trimethylpentane
*n*Heptane

Three principal procedures have been employed thus far in preparing hydrocarbons as follows:

a. A mixture of olefins having the desired skeletal structure is produced by dehydration of the appropriate tertiary carbinol. If the three alkyl groups of the carbinol are the same, a single olefin is obtained; otherwise the mixture is difficult to separate into its components. The carbinol is synthesized by the reaction of a Grignard reagent with a ketone or ester, the Grignard reagent being formed by the action of an alkyl halide on metallic magnesium in dry ether. This reaction briefly may be formulated as follows:

$$R-\overset{\overset{O}{\parallel}}{C}-R'' + R''MgX \rightarrow R-\overset{\overset{R''}{|}}{\underset{\underset{R''}{|}}{C}}-OH$$

Where: R, R', and *R"* are alkyl groups, and *X* is a halogen. It is necessary to add the ketone or ester in ether slowly to the Grignard reagent because of the large amount of heat produced. If desired, the olefin (or mixture of olefins) may be hydrogenated to form a saturated hydrocarbon.

b. This method also makes use of the Grignard reaction. However, the olefin is produced directly by the reaction of the appropriate alkylmagnesium halide with an allyl-type unsaturated halide. The reaction briefly may be formulated as follows:

$$H_2C=\underset{\underset{R}{|}}{C}-\underset{\underset{H_2}{|}}{C}-X + R'MgX \rightarrow H_2C=\underset{\underset{R}{|}}{C}-\underset{\underset{H_2}{|}}{C}-R + MgX_2$$

Where: R is an alkyl group or hydrogen, and *X* is a halogen. The olefin thus formed may be hydrogenated, if desired, to the corresponding paraffin.

c. Direct hydrogenation, using a nickle catalyst, also is employed to convert aromatics to the corresponding cyclohexane derivatives.

Other procedures undoubtedly will be employed in the course of time. It is possible, however, to prepare a great many hydrocarbons of the various types by appropriate combinations of the above methods. The first method has been used most extensively up to the present.

Very few reactions can be trusted to give pure products, with the result that certain steps are necessary in order to insure that the resulting hydrocarbons will be of satisfactory purity. A procedure which largely is standardized has been employed as follows:

a. Fractionation of the crude olefin through one of the metal total-reflux columns.
b. Examination of the main fraction for residual halide, ketone, or ester, and chemical treatment for their removal if present.
c. Hydrogenation.

d. Refractionation collecting as "heads," "main fraction," and "tails," and examining each for residual olefin or other impurities.
e. Rehydrogenation over fresh catalyst.
f. Washing with strong sulfuric acid, if necessary.
g. Final distillation through all-glass columns collecting in 100-ml. portions, and constructing distillation and refractive-index curves.

The degree of purity (for paraffins) is determined by the following tests:

a. Absence of halides (modified Beilstein test).
b. Insolubility in concentrated sulfuric acid.
c. Absence of unsaturation (bromine test).
d. Absence of peroxides (acidified potassium-iodide test).
e. Flat distillation curve (no more than 0.1° C. on accepted portion of curve).
f. Flat refractive-index curve (no more than 0.0001 variation in n^{20}_D on accepted portion of curve).
g. Flat, reproducible freezing and melting curves.

At the end of the first year of operation, the hydrocarbon laboratory had the following equipment available:

Four Grignard reactors:
  One 3-gal. capacity (copper lined).
  One 5-gal. capacity (steel).
  Two 15-gal. capacity (steel).
Four metal total-reflux columns (40-45 plates).
Eight still pots (interchangeable on above columns):
  Three 1.5-gal. capacity.
  Three 3-gal. capacity.
  Two 5-gal. capacity.
  Three all-glass total-reflux columns (23-28 plates).
  One cracking still and furnace.
  One chemical washer.
  One refrigerating unit for control of reactors and condensers.
  One mechanical refrigerator (old).

In addition to the above, the laboratory has the use of the following equipment provided by the university:

One American Instrument Company super-pressure autoclave, 3000-ml. capacity and with automatic thermostatic control.
One Abbe refractometer.
One freezing-point–melting-point apparatus with Leeds and Northrup Micromax recorder.

This equipment is installed in the main chemistry building, a large laboratory room having been made available for this purpose. Figures 2, 3, and 4 show the more important apparatus items and their installation.

Plans for the second year of the program provide for the construction of a small building to house the large Grignard reactors and such other apparatus as is deemed too large for proper operation in the main laboratory building, as shown in Figure 5. It is planned also to extend the distillation equipment, and to add another hydrogenator. With these additions, it is anticipated that about 40 hydrocarbons can be prepared and purified during this year, in quantities suitable for engine-combustion studies and physical- and thermal-property determinations.

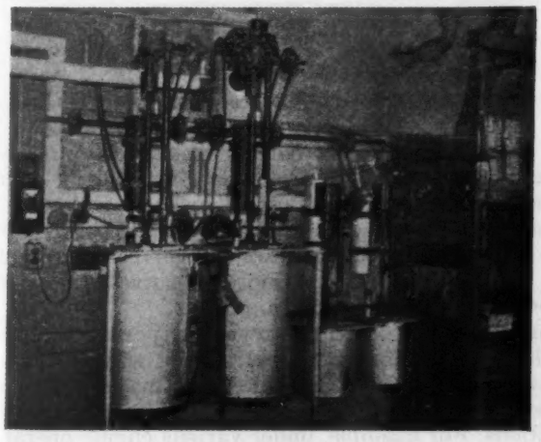

FIGURE 2
Grignard Reactors

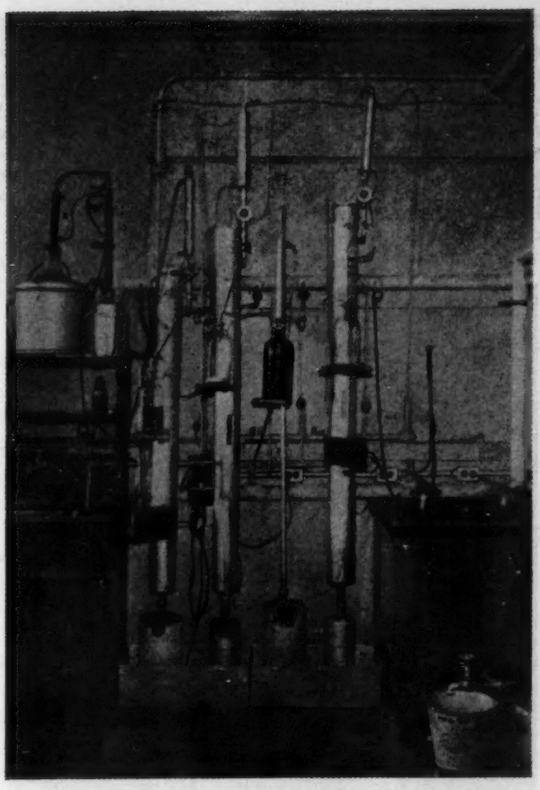

FIGURE 3
40-45 Plate Total-Reflux Columns

ENGINE-COMBUSTION STUDIES

In the organizing of the program, the General Motors Research Laboratories accepted the assignment of carrying out the engine research program. During the first year this activity was supervised by T. A. Boyd, with direct assistance from W. G. Lovell and J. M. Campbell. During the second year the work is being continued by Lovell and Campbell. The procedures employed for the basic studies were developed by the Fuel Section of the General Motors Research Laboratories, and are discussed as follows:

General problem of knock measurement: On account of the importance of anti-knock quality in determining the potential usefulness of a fuel in the conventional spark-ignition engine, the measurement of knocking tendency is an important phase of this investigation. This problem is complicated greatly by the fact that the relative knocking tendencies of different fuels change with changes in engine conditions. This is particularly true of pure hydrocarbons, in which the characteristics of each hydrocarbon are not obscured by the presence of other materials. It, therefore, has been desirable to obtain as broad a foundation of knowledge of the knocking characteristics of each hydrocarbon as possible.

Conventional ASTM and CFR research knock tests: As a first step in this direction, the octane numbers of each hydrocarbon are to be determined by the conventional ASTM test, D 357-39, and by the CFR research

(1939) method of test. This part of the program involves the following tests by each method:

1. Octane numbers on pure hydrocarbon.
2. Lead susceptibilities in concentrations of 1.0 ml. and 3.0 ml. of tetraethyl lead per U. S. gallon, when ASTM and research octane numbers can be obtained.
3. Blending octane numbers for fuels of 70 octane number, or higher, by the ASTM method in a 20-percent concentration in a base fuel composed of 60 percent *iso*octane and 40 percent *n*heptane.

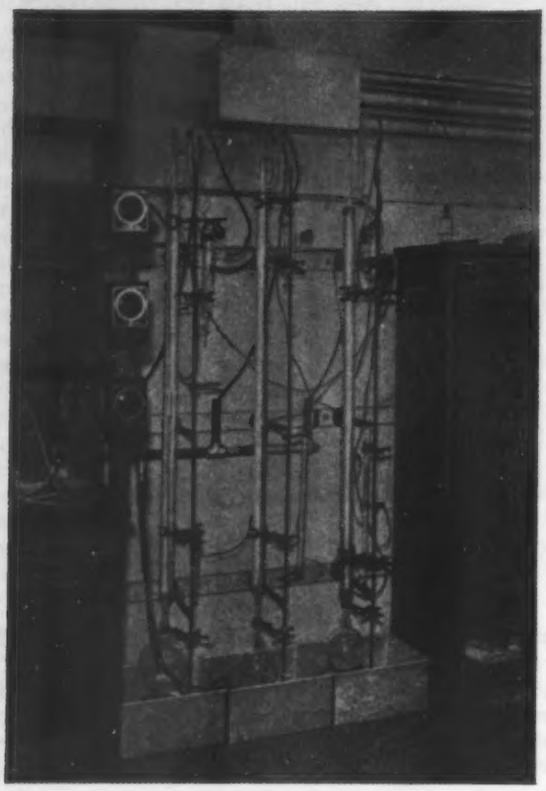

FIGURE 4
23-28 Plate Total-Reflux Columns

These tests require approximately 2000 ml. of fuel.

The results obtained by these two methods of test are expressed in octane numbers, whenever possible; and, consequently, have the advantage of a terminology that is in familiar use. However, both of these methods were developed especially for, and best are suited for, rating commercial gasolines in the limited octane range between approximately 50 and 85 octane number. The application of these methods to fuels outside of this range of octane numbers—particularly to fuels above 100 in octane number—has not been altogether satisfactory, for a number of reasons. This has been partly because of limitations in the instrumentation; partly because of limitations of the reference fuels; and partly because of the arbitrary combination of engine speed, mixture temperature, and ignition timing in the ASTM procedure for the purpose of producing a given effect, viz., an approach to correlation with road-test ratings.

Development of procedure for additional knock tests: In order to broaden the scope of the knock tests beyond that afforded by the conventional ASTM and CFR research methods, considerable attention has been given to the development of a test procedure that seems better suited to the exploratory nature of this project. At the same time, it has been recognized that our present knowledge of this entire problem of technique in knock measurement is very incomplete, and will be subject to revisions in viewpoint as new concepts develop. Under these circumstances a simple, direct, and workable procedure was needed which could be expected to be a reasonably-satisfactory guide to further progress in the study of fuels.

After considerable discussion of both supercharging and variable-compression methods, a decision has been reached in favor of the variable-compression or critical-compression ratio technique for the present. One of the principal objections to the supercharging method is the comparatively-large amount of fuel required in each test. Another problem in connection with supercharging was the question that existed as to whether the supercharging technique had yet been developed sufficiently to warrant its use in this program at this time.

Critical-compression-ratio tests: The general scheme of approach that is being followed in the determination of knocking characteristics by critical-compression tests is illustrated by some data which were obtained during the course of the development of this procedure. These data are presented in Figure 6, and include *iso*octane,[1] di*iso*butylene,[2] triptane (2,2,3-trimethylbutane),[3] and several blends of di*iso*butylene and benzol, respectively, in a nominal 74-octane-number base gasoline.

These data indicate clearly the exploratory nature of these combustion studies, and illustrate some of the fundamental fuel characteristics that may be expected in varying degrees among the pure hydrocarbons that will be studied in the normal course of this project. For example, the relation of the knocking tendency to changes in engine speed varies widely for different fuels. *Iso*octane, and the nominal 74-octane base gasoline, as well as a blend containing 75 percent of benzol in the same gasoline, appeared to have less tendency to knock as the speed was increased from 600 r.p.m. to

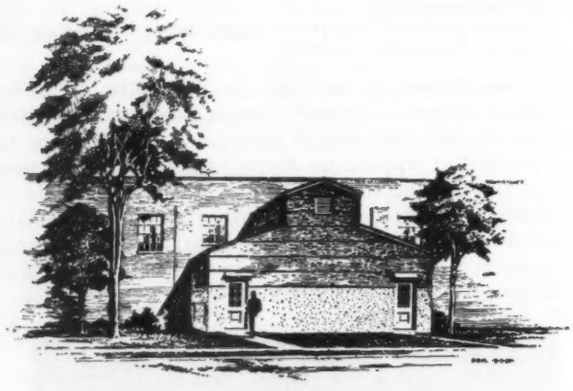

FIGURE 5
Hydrocarbon Laboratory (Architect's Sketch)

2000 r.p.m. On the other hand, di*iso*butylene, and even triptane—a paraffin hydrocarbon which might be expected to react like *iso*octane—knocked more with an increase in engine speed. All of the fuels knocked more when the operating temperature was increased, although some fuels were distinctly more sensitive to a change in operating temperature than others.

The net result of these varying responses to engine speed and operating temperatures is a wide variety of relative knocking characteristics that may be observed between a given group of fuels under different operating conditions. For example, under various engine operating conditions designated, the changes in relative anti-knock value between *iso*octane, di*iso*butylene, and a blend con-

[1]Reference fuel S-1; [2]Roehm and Haas; [3]Sample of high purity supplied by Ethyl Gasoline Corporation.

taining 75 percent benzene in a nominal 74-octane-number base gasoline were as follows, in the order of decreasing degree of freedom from knock:

Method 1	Method 2	Method 3	Method 4
Diisobutylene	Diisobutylene	75% benzol	*Iso*octane
75% benzol	*Iso*octane	*Iso*octane	75% benzol
*Iso*octane	75% benzol	Diisobutylene	Diisobutylene

These variations in the relative anti-knock value of three different fuels under four arbitrarily-selected engine conditions, which are shown qualitatively and quantitatively in Figure 6, indicate the complexity of the problem when it is examined in detail. This is even more apparent when it is recognized that around each point in Figure 6, representing the characteristics of a single fuel under specified engine conditions, there can be developed an entirely new figure representing the effect of such important variables as ignition timing, mixture ratio, lead susceptibility, and of various blending materials. A partial development along these lines and pertaining to mixture ratio and lead susceptibility,

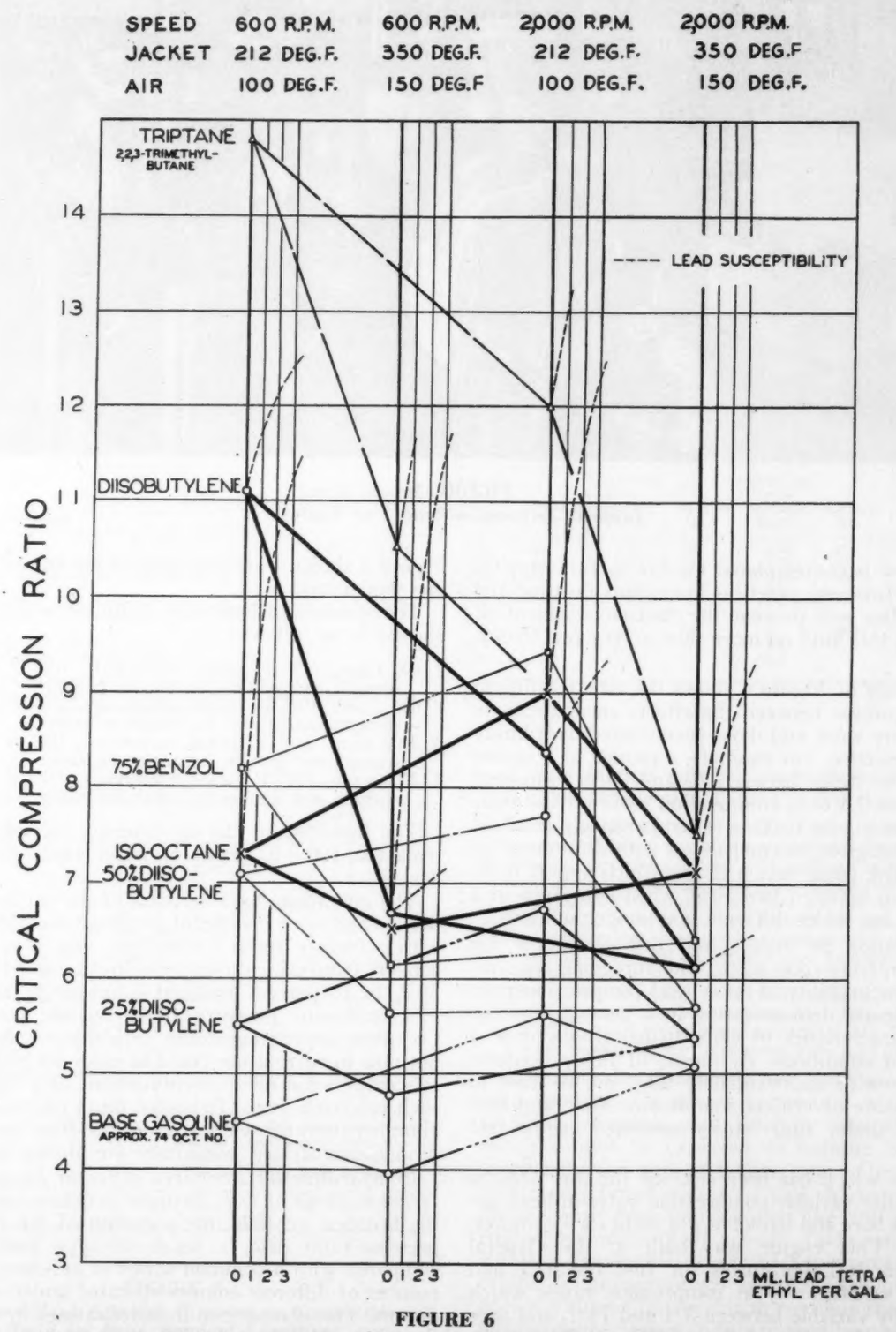

FIGURE 6

Variation in Critical Compression Ratio of Six Fuels for Four Standard Test Conditions

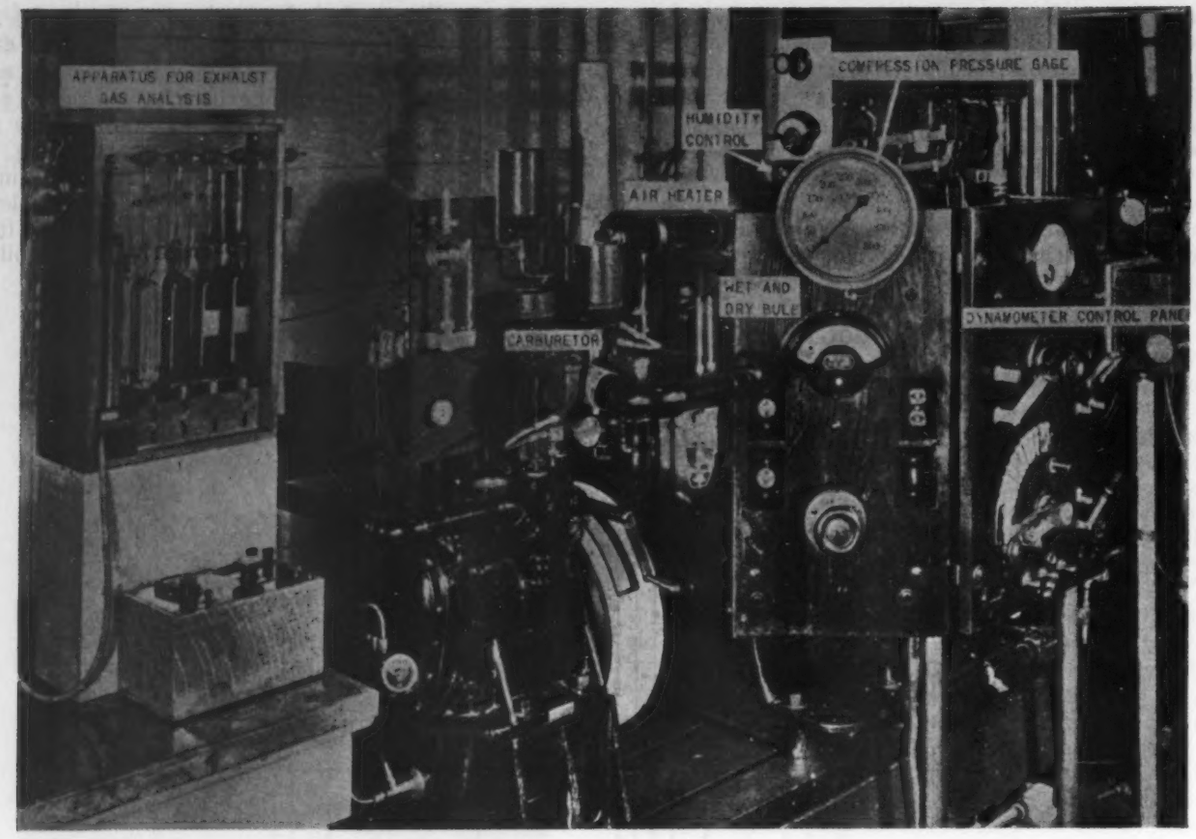

FIGURE 7
Critical-Compression-Ratio Test Engine

of course, now is contemplated insofar as fuel supplies will permit. However, practical limitations on time and on fuel supplies will prevent the fuel development of knowledge of this kind on more than a very few hydrocarbons.

Further study of Figure 6 shows the totally different order in magnitude between the effects encountered in this exploratory work and those encountered in ordinary commercial practice. For example, a change of 5 octane numbers in the range between 70 and 80 is equivalent to from 0.2 to 0.3 of a compression ratio on the scale represented in Figure 6. This is comparatively small, if not almost negligible, in comparison with differences of from one to five compression ratios, which appear to be not uncommon between two fuels when compared in a single engine but under different operating conditions.

Standardization of engine and test procedure for critical-compression-ratio tests: The foregoing tests indicated the practicability of the critical-compression-ratio method of clearly demonstrating in a general way the knocking characteristics of pure hydrocarbons over a wide range of conditions. By means of this procedure, it is possible with approximately 2000 ml. of fuel to obtain a measure of critical compression ratio and lead susceptibility under four widely-separated engine test conditions.

The engine which has been selected for this work is a single-cylinder variable-compression valve-in-head engine, having a bore and stroke of 3¼ inches x 4½ inches, respectively. This engine was built at the General Motors Research Laboratories for fuel research, and will operate satisfactorily at compression ratios which are continually variable between 3:1 and 15:1, and over a range of speeds varying between 600 and 2000 r.p.m. Figure 7 shows a general view of the engine and auxiliary apparatus.

The schedule of basic test conditions which have been chosen is as follows:

1. 600 r.p.m., 212° F. jacket temperature, 100° F. air, mixture strength and ignition for maximum power.
2. 600 r.p.m., 350° F. jacket temperature, 150° F. air, mixture strength and ignition for maximum power.
3. 2000 r.p.m., 212° F. jacket temperature, 100° F. air, mixture strength and ignition for maximum power.
4. 2000 r.p.m. 350° F. jacket temperature, 150° F. air, mixture strength and ignition for maximum power.

The humidity of the air entering the engine is controlled at 100±10 grains of water vapor per pound of dry air.

The operating characteristics of the engine have been determined over the useful range of compression ratios with reference fuels. From these data it is possible to convert from critical compression ratio to percent S-1 in M-2, or to percent certified *iso*octane in *n*heptane, or to compression pressure, or to relative power output. Complete interchangeability with other reference fuels not now in current use could be made by means of critical-compression-ratio determinations of a few blends of such reference fuels. Indicated mean effective pressures obtained from this engine under the four operating conditions enumerated previously are shown in Figure 8.

Comparative tests between different engines and different methods of test: In order to obtain some basis for the broadest possible interpretation of the critical-compression-ratio data, a series of type fuels has been compared with a common series of reference fuels in a number of different engines operated under various conditions. This comparison includes ratings by the ASTM, the CFR research, and CFR-AFD methods 1-a and 1-b,

TABLE 1
Comparison of Different Test Engines
(Ratings Expressed as Percent S-1 in M-2[9])

FUEL	FROM CRITICAL COMPRESSION RATIOS[1]				FROM SUPER-CHARGED ENGINES: 2⅝-in. x 4½-in. Engines[2]			3¼-in. x 4½-in. Engine[3]	CFR Research[4]	ASTM[4]	AFD† Full Scale Aircraft[5]
Speed, r.p.m.	600	600	2,000	2,000	600	900	1,800	1,800	600	900	
Jacket temperature, °F.	212	350	212	350	200	200	350	350	212	212	
Air temperature, °F.	100	150	100	150	110	110	110	110	100	300[6]	
74-octane base gasoline	70	71	72	73	74	70	75	74	71	71	....
74-octane gasoline plus 3.0 ml. tetraethyl lead	87	90	94	93	90	89	91	92	88	88	90 to 92
75 percent benzol in 74-octane base gasoline	0.25[7]	98	0.1[7]	93	149[8]	3.9[7]	0.25[7]	0.8[7]	0.4[7]	92	84
25 percent di*iso*butylene in 74-octane base gasoline	86	87	86	80	90	89	88	88	88	80	80
50 percent di*iso*butylene in 74-octane base gasoline	99	95	93	84	0.5[7]	0.4[7]	95	96.5	99	84	80
Di*iso*butylene	2.7[7]	100	97	87	170[8]	177[8]	0.5[7]	0.6[7]	0.5[7]	86	....
50 percent 74-octane base gasoline, 40 percent S-1, 10 percent *iso*pentane, 3.0 ml. tetraethyl lead	99	99	0.2[7]	0.3[7]	98	100	100	0.28[7]	98	100	100 to 100+0.5

[1] 3¼-in. x 4½-in. variable-compression engine at General Motors, research laboratories division; ignition and mixture for maximum power.
[2] Compression ratio, 5.5:1; ignition temperature, 20° b.t.c.* at 600 r.p.m., 30° at 900 and 1,800 r.p.m.; mixture for maximum thermal-plug temperature; compression-ignition piston, Ethyl Gasoline Corp.
[3] Compression ratio, 7.0:1; ignition temperature, 30° b.t.c.; mixture for maximum army-type 15-plug temperature; aluminum piston, Standard Oil Co. (Indiana).
[4] Average of ratings from two laboratories.
[5] Specifications given by CFR aviation-fuels division based on the minimum ratings found in full-scale engines.
[6] 300° F. mixture temperature.
[7] Milliliters of tetraethyl lead per gallon of S-1. Certified *iso*octane in research and ASTM procedure.
[8] Percent boost pressure permissible with S-1.
[9] S-1 is technical *iso*octane having an ASTM octane number of 100; M-2 is a gasoline having an ASTM octane number of 19.
* Before true center. † Aviation-fuels division.

TABLE 2
Summary of Knock Tests on Three Hydrocarbons

HYDROCARBON	ASTM Octane No.*	Research Octane No.*	GENERAL MOTORS ENGINE: 600 R.P.M. 212° F. Jacket Temperature		600 R.P.M. 350° F. Jacket Temperature		2,000 R.P.M. 212° F. Jacket Temperature		2,000 R.P.M. 350° F. Jacket Temperature	
			Critical Compression Ratio	Octane No.*	Critical Compression Ratio	Octane No.*	Critical Compression Ratio	Octane No.*	Critical Compression Ratio	Octane No.*
Ethyl cyclohexane	40.8	45.6	3.55	36	2.80	32	4.35	37	4.00	45
Ethyl cyclohexane plus 1.00 ml. tetraethyl lead	52.3	51.3	3.80	49	3.00	47	4.75	54	4.25	55
Ethyl cyclohexane plus 3.0 ml. tetraethyl lead	65.4	65.4	4.10	61	3.45	62	5.35	70	4.75	69
Ethyl benzene	97.9	0.8†	13.50	...	8.20	...	9.3	...	6.9	97
Ethyl benzene plus 1.0 ml. tetraethyl lead	100	0.8†	15.10	...	9.10	...	11.4	...	7.8	...
Ethyl benzene plus 3.0 ml. tetraethyl lead	0.2†	0.8†	...	...	11.00	...	...	...	8.6	...
*Iso*octane (S-1)	...	...	7.30	100	6.60	99	9.1	99.5	7.1	99
*Iso*octane plus 1.0 ml. tetraethyl lead	...	...	9.60	...	8.80	...	10.5	...	8.0	...
*Iso*octane plus 3.0 ml. tetraethyl lead	...	...	11.20	...	11.50	...	12.3	...	9.1	...

* Equivalent percent *iso*octane in *n*heptane for each corresponding engine condition.
† Milliliters of tetraethyl lead in certified *iso*octane.

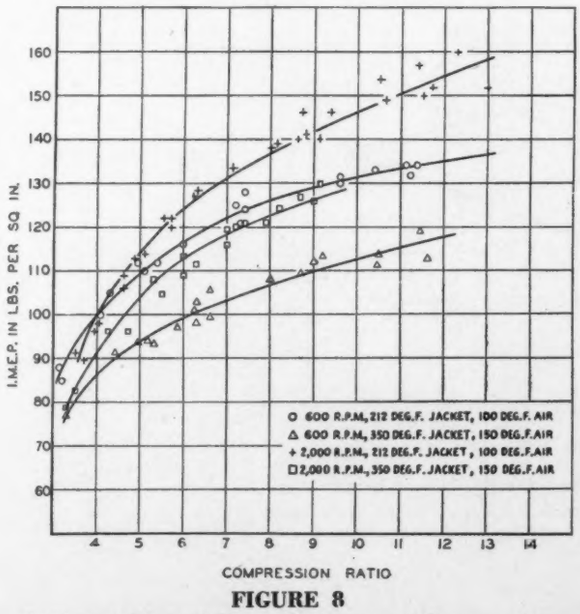
I.M.E.P. IN LBS. PER SQ. IN.
COMPRESSION RATIO
○ 600 R.P.M., 212 DEG.F. JACKET, 100 DEG.F. AIR
△ 600 R.P.M., 350 DEG.F. JACKET, 150 DEG.F. AIR
+ 2,000 R.P.M., 212 DEG.F. JACKET, 100 DEG.F. AIR
□ 2,000 R.P.M., 350 DEG.F. JACKET, 150 DEG.F. AIR

FIGURE 8
Indicated Mean Effective Pressure vs. Compression Ratio for Four Standard Conditions

and tests in two different supercharged engines. The results are tabulated in Table 1. These data indicate that:

1. No single set of tests by the critical-compression method agrees with any one of the supercharged tests.
2. That the supercharged tests with different engines agreed when similar operating conditions were used, but under different conditions of operation the data are not comparable.
3. Only the CFR-AFD methods 1-a and 1-b, which do not employ supercharging, show good agreement with the ratings specified by the CFR Aviation-Fuels Division for correlation with full-scale engine tests.
4. The closest approach to such correlation, however, by the critical-compression-ratio tests was obtained at 2000 r.p.m., 350° F. jacket temperature, and 150° F. air. The latter ratings were usually in fair agreement with ASTM ratings.

Although the six engine-test conditions which have been specified for use in connection with this project (ASTM, research, and four by critical compression ratio) cannot be expected to indicate the usefulness specifically for any particular type of engine, they do give a very broad survey of fuel characteristics. In addition, these data indicate that the full-scale aircraft-engine performance of specific fuels can be estimated within a reasonable degree of approximation from the critical-compression-ratio tests. At the present time it does not appear practicable to continue the supercharged tests in connection with this project because of the large

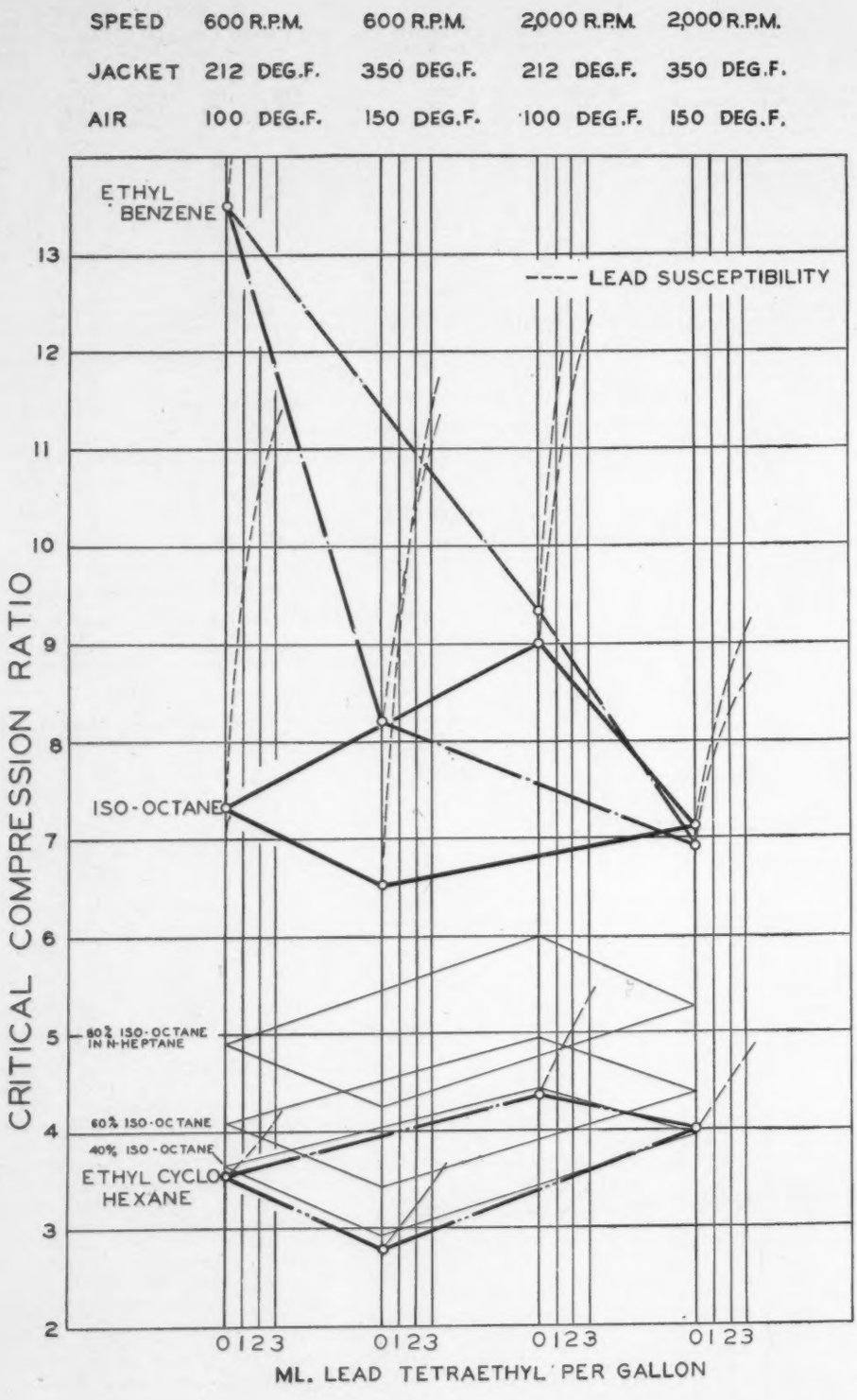

FIGURE 9

Variation in Critical Compression Ratio, for Four Standard Test Conditions, for Ethyl Benzene, Ethyl Cyclohexane, and Isooctane (2,2,4-Trimethylpentane)

amounts of fuel which would be required. However, it later may prove desirable to make supercharged tests on some particular hydrocarbons which appear especially interesting in subsequent work.

Typical results: Some data which have been obtained already on certain hydrocarbons prepared at Ohio State University for use in this project are shown in Figure 9 and in Table 2. Figure 9, which is similar to Figure 6, shows a wide range in relative knocking characteristics among hydrocarbons of different molecular structure and containing eight carbon atoms.

PHYSICAL AND THERMAL PROPERTIES

As indicated earlier in this paper, no specific arrangements have been made for the physical- and thermal-property program. Instead it is planned to make the hydrocarbons available to individuals who are specializing in the particular fields involved, and who may be in a position to cooperate in the work of the hydrocarbon project. The general plan adopted is outlined as follows:

At least 500 ml. of the best portion of each purified hydrocarbon will be set aside for the determination of physical properties. The purity of this cut will be scrutinized further; and, if advisable, additional purification will be effected by one or more appropriate methods: chemical treatment, fractional distillation, or fractional crystallization. The properties which it is desired to determine are listed hereinafter, and have been divided into two groups—in which group 1 contains properties which probably are related to combustion characteristics fundamentally, and group 2 contains those properties of general scientific and engineering interest which should be determined, if possible, while the pure hydrocarbons are available.

Group 1

1. Heat of combustion.
2. Heat capacity down to liquid hydrogen temperatures (including determining heat of fusion).
3. Heat capacity and thermal conductivity of gaseous phase.
4. Heat of vaporization.
5. Vapor pressure.
6. Infrared absorption spectra, particularly in the range, 1 to 12μ.
7. Raman spectra.
8. Ultraviolet absorption in the Schumann region.

Group 2

9. Refractive index at several temperatures.
10. Refractive dispersion at several temperatures.
11. Density at several temperatures, including 20° C.
12. Liquid viscosity at several temperatures.
13. Vapor viscosity.
14. Critical temperature of solution in aniline.

Although no hydrocarbons have been shipped for the purpose, the project has agreed to furnish materials to the following:

1. F. J. Rossini, National Bureau of Standards, for the determination of the *heats of combustion.*
2. Emma Carr for determination of *ultraviolet absorption spectra.*
3. A. V. Grosse for certain octanes to complete *Raman spectra measurements.*
4. H. M. Randall of the University of Michigan *for infrared spectrographic studies.*

The cooperation of the National Bureau of Standards had been enlisted in the determination of the heats of combustion, and probably the vapor pressure. Arrangements have been made with other departments of Ohio State University for the determination of some of the other properties, and negotiations are under way with other interested parties for the balance. These determinations require only very small quantities of material, and in most cases the hydrocarbon is still available for other purposes after its use. It is hoped, therefore, that other qualified laboratories will express interest in securing samples of the hydrocarbons for determining other properties. Such requests will be considered carefully by the committee on the basis of the qualifications of the applicants, as well as the probable usefulness of the data to be secured. Additional properties which would seem to be of interest are dielectric constants, dipole moments, surface tensions, PVT* relationships, etc.

* Pressure-volume-temperature.

CONCLUSION

In conclusion, it is pointed out that the API hydrocarbon research project has been formed to make as complete a study as possible of the engine-combustion, physical and thermal properties of the gasoline-range hydrocarbons. A laboratory organization has been established at Ohio State University to prepare the required hydrocarbons; the Research Laboratories of the General Motors Corporation have undertaken the engine research program; and plans have been formulated to make materials available to appropriate specialists for physical- and thermal-property determinations. The project now is entering upon the second year of an anticipated four-year program. A number of hydrocarbons have been procured or prepared, and subjected to the examination in the basic engine program. The engine-study procedure has been explored thoroughly; and, as finally adopted for the project, is shown to cover a very wide range of engine conditions, and to be capable of producing results which are indicative of basic knocking tendencies. This work is proceeding as rapidly as the hydrocarbons become available.

The purpose of this report is to outline the objectives and procedures employed by the API hydrocarbon research project. With its submission, the duties of the chairman with regard to presentation of the work of the project may be considered as largely fulfilled. It is anticipated that future reports will present specific data, and will be presented by the individuals most closely concerned.

APPENDIX I

COMMITTEE ON HYDROCARBON RESEARCH

Chairman: D. P. Barnard, Standard Oil Company (Indiana), Whiting, Ind.
E. G. Borden, Power Patents Co., New York, N. Y.
R. E. Burk, The Standard Oil Co. of Ohio, Cleveland, Ohio.
*G. H. Burruss, Anderson-Prichard Oil Corp., Oklahoma City, Okla.
George Calingaert, Ethyl Gasoline Corp., Detroit, Mich.
*B. P. Crittenden, Rodessa Oil and Refining Co., Shreveport, La.
D. E. Day, Richfield Oil Co., Los Angeles, Calif.
Gustav Egloff, Universal Oil Products Co., Chicago, Ill.
S. W. Ferris, The Atlantic Refining Co., Philadelphia, Pa.
E. W. Gard, Union Oil Co. of California, Los Angeles, Calif.
J. M. Gardiner, Republic Oil Co., Pittsburgh, Pa.
R. A. Halloran, Standard Oil Co. of California, San Francisco, Calif.
J. Bennett Hill, Sun Oil Co., Philadelphia, Pa.
W. E. Kuhn, The Texas Co., New York, N. Y.
*B. H. Lincoln, Continental Oil Co., Ponca City, Okla.
W. G. Lovell, General Motors Corp., Detroit, Mich.
†J. T. McCoy, Tide Water Associated Oil Co., Bayonne, N. J.
J. B. Macauley, Chrysler Corp., Detroit, Mich.
A. E. Miller, Sinclair Refining Co., New York, N. Y.
C. W. Montgomery, Gulf Research and Development Co., Pittsburgh, Pa.
*W. E. Moody, Deep Rock Oil Corp., Cushing, Okla.
E. V. Murphree, Standard Oil Development Co., New York, N. Y.
†G. G. Oberfell, Phillips Petroleum Co., Bartlesville, Okla.
†J. T. Poole, Lion Oil Refining Co., El Dorado, Ark.
J. B. Rather, Socony-Vacuum Oil Co., Inc., New York, N. Y.
H. V. Smith, The Barber Co., Philadelphia, Pa.
S. Tijmstra, Shell Development Co., Emeryville, Calif.
C. R. Wagner, The Pure Oil Co., Chicago, Ill.

* First year.
† Second year.

Partial Volumetric Behavior of the Lighter Paraffin Hydrocarbons in the Gas Phase

API Research Project 37

B. H. SAGE and W. N. LACEY

California Institute of Technology, Pasadena, California

THE necessity of predicting the volume which a given amount of hydrocarbon gas would occupy under a wide range of conditions of temperature and pressure frequently is met in the production, transportation, and processing of natural gas. This paper proposes a method of making such predictions for cases in which a fractionation analysis of the gas is available. The method is tested by application to several cases for which both composition and volumetric behavior have been determined experimentally.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

(The statements and opinions expressed herein are those of the author, and should not be construed as an official action or opinion of the Institute nor of this publication.)

THE prediction of the volumetric behavior of complex hydrocarbon gases is of value in many industrial calculations. A number of attempts have been made to predict such behavior for both simple and complex gaseous mixtures. Beattie[1] proposed the use of an equation of state in which the constants were related simply to the composition. This method was found to yield results in accord with experimental data for mixtures of nitrogen and methane.[2] Masson and Dolley[3] attempted to relate the pressure exerted by a gaseous mixture to that exerted by the components individually at the same temperature and total volume. Gilliland[4] proposed a method of predicting the volumetric behavior of gaseous mixtures involving the correlation of the slopes and intercepts of the isochors of the components on a pressure-temperature diagram. This method appears to yield satisfactory results in the case wherein the components exist in the gas phase in the pure state when at the same temperature and molal volume as for the mixture. Another general method of attack proposed by Kay[5] involved the estimation of the "pseudo-critical state" for the gas in question and the subsequent estimation of its volumetric behavior from the law of corresponding states.

In the present paper a somewhat different approach has been attempted. The behavior of a number of the lighter components of naturally-occurring gaseous hydrocarbons in several binary mixtures has been studied. These data afford an incomplete empirical background upon which to base a method of prediction of the behavior of complex hydrocarbon mixtures. It should be realized that at the present time there are insufficient data to permit such predictions to be made with accuracy.

GENERAL CONSIDERATIONS

In considering the volumetric behavior of gaseous mixtures in terms related to the behavior of their components, it is convenient to employ partial quantities.[6] Such quantities have been proposed already for the correlation of the volumetric behavior of complex hydrocarbon mixtures in the liquid phase.[7] The partial specific volume of any component k, as it will be employed in the present discussion, may be defined by the following equation†:

$$\bar{V}_k = \left(\frac{\partial V}{\partial m_k}\right)_{T,P,m_i} \qquad (1)$$

† See nomenclature at end of the paper.

Equation (1) indicates that a partial specific volume represents the change in volume of a large quantity of a system of variable weight under isothermal, isobaric conditions due to the addition of a unit weight of the component in question. The equation stipulates by the use of the subscript m_i that the weight of all components other than component k must be maintained constant during the change in state.

It follows from the definition of a partial quantity that the specific volume of a mixture is related to the composition and the partial specific volume of each of the components by means of an equation of the following form[8]:

$$V = \sum_{k=1}^{k=n} \bar{V}_k n_k = \bar{V}_1 n_1 + \bar{V}_2 n_2 + \ldots + \bar{V}_n n_n \qquad (2)$$

In order that equation (2) may be applicable, it is necessary that the partial volume used for each component be the value applying to the mixture at the state in question. Strictly speaking, the partial volume of a component is a function of the state of the phase, and varies, therefore, with changes in any of the variables which establish this state.

In the case of gases, the partial specific volumes of the components undergo large changes with variations of both temperature and pressure. For this reason it is advantageous to employ "residual methods." In the case of gas phases, the residual volume conveniently

is defined in relation to the specific volume, and the reference volume by means of the following relationship:

$$V = V_R - \underline{V} = \frac{bT}{P} - \underline{V} \qquad (3)$$

If it is desired to consider a system of variable weight, equation (3) assumes the following form:

$$\underline{V} = \frac{mbT}{P} - m\underline{V} \qquad (4)$$

If equation (4) is applied to an *n*-component system of variable weight, it may be rewritten in the expanded form:

$$\underline{V} = (m_i b_i + m_k b_k)\frac{T}{P} - (m_i + m_k)\underline{V} \qquad (5)$$

If equation (5) is differentiated while holding constant the temperature, pressure, and weight of all components other than component *k*, the following relationship is obtained:

$$\bar{V}_k = \left(\frac{\partial \underline{V}}{\partial m_k}\right)_{T,P,m_i} = \frac{b_k T}{P} - \underline{V} - (m_i + m_k)\left(\frac{\partial \underline{V}}{\partial m_k}\right)_{T,P,m_i} \qquad (6)$$

By suitable substitution equation (6) may be rewritten in the following more useful form:

$$\bar{V}_k = \frac{b_k T}{P} - \left[\underline{V} + (1 - n_k)\left(\frac{\partial \underline{V}}{\partial n_k}\right)_{T,P}\right] \qquad (7)$$

It is of interest to investigate the geometric significance of the portion of this equation included in the brackets. In Figure 1 are presented the residual volumes for mixtures of methane and ethane at 160° F. for a series of pressures.[9] These data indicate significant departures from the behavior of ideal solutions even at infinite attenuation. The line **AB** is drawn tangent to the isobar for 1000 pounds per square inch at a composition of 60 weight percent methane. The ordinate value of the intercept **A,** which corresponds to the composition of pure methane, is equal to the terms within the brackets of equation (7) when methane is taken as component *k*. This follows, since the ordinate at the point of tangency is the residual volume at this state, whereas the slope of the line **AB** is equal to $\left(\frac{\partial \underline{V}}{\partial n_k}\right)_{T,P}$ and the distance from the point of tangency to the right-hand ordinate corresponds to the term $1-n_k$. From the geometry of the figure it is then evident

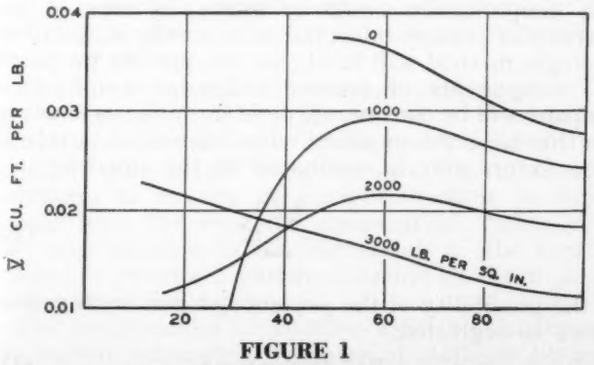

FIGURE 1

Residual Specific Volumes for the Methane-Ethane System at 160° F.

that the intercept ordinate value is equivalent to the sum of the last two terms in question.

For convenience, and by analogy from specific partial quantities, such an intercept value[10] will be called the "residual partial specific volume." In this instance the intercept with the right-hand ordinate is the residual partial specific volume of methane in the gas phase of the methane-ethane system at a composition of 60 weight percent methane and at 1000 pounds per square inch and 160° F. Likewise the intercept with the left-hand ordinate corresponding to pure ethane would be the residual partial specific volume of ethane in the same system at the same state. Equation (7) may be rewritten in the following simple form:

$$\bar{V}_k = \frac{b_k T}{P} - \bar{\underline{V}}_k \qquad (8)$$

The residual partial specific volumes of the components of gaseous mixtures are convenient quantities to employ, as they do not vary greatly with either temperature or pressure and, therefore, permit the use of relatively-simple interpolation. In addition, this quantity represents only a small part of the partial specific volume, and this reduces the need for high-percentage accuracy in its estimation.

A combination of equations (2) and (8) yields the following expression for the specific volume of a multi-component gaseous mixture in terms of its composition and the residual partial specific volumes of the components:

$$V = \sum_{k=1}^{k=n}\left(\frac{b_k T}{P} - \bar{\underline{V}}_k\right)n_k \qquad (9)$$

From a consideration of equation (9) and Figure 1 it is apparent that, at low pressures, the first term which corresponds to the perfect gas volume of the mixture contributes a large fraction of the whole. Therefore, at low pressures the volume of the hydrocarbon gases may be predicted with reasonable accuracy, even though there is rather a large percentage of uncertainty in the establishment of the residual partial specific volume of the components.

EXPERIMENTAL BACKGROUND

In order to make use of the relationships derived in the preceding section, it is necessary to have a knowledge of the partial volumetric behavior of each of the components as a function of the state of the gaseous mixture in question. At the present time there are no data available to the authors relating to the partial specific volume of the lighter components in complex hydrocarbon mixtures. However, information concerning the behavior of a number of binary gaseous-hydrocarbon mixtures has become available recently.[11, 12, 13] As a tentative procedure it is possible to consider the partial volumetric behavior of the lighter paraffin-hydrocarbon constituents in these binary systems as directly applicable to the behavior of complex hydrocarbon gases. It should be realized that this assumption inevitably introduces errors in the resulting predictions of the specific volume of the complex mixtures. However, it is believed that such uncertainties are sufficiently small in many instances to make the predictions of engineering value. Furthermore, the method will increase in value

as more experimental knowledge of partial volumetric behavior accumulates.

Experimental data are available concerning the volumetric behavior of pure methane,[2, 14] ethane,[15, 16] propane,[17, 18] and *n*butane[19, 20] in the gaseous region throughout the temperature interval of interest in petroleum-production practice. These data serve to establish the behavior in the pure state of these important constituents of dry natural gases with an accuracy adequate for most engineering purposes.

The behavior of mixtures of methane and ethane throughout the entire composition range at pressures up to 3000 pounds per square inch in the temperature interval between 70 and 250° F. is known.[12] These data have been employed in the present instance to establish the partial volumetric behavior of methane and of ethane in the methane-ethane system. The residual partial specific volume of methane in this system is presented in Figure 2 as a function of composition at 160° F. The residual partial specific volume of methane is equal to its residual specific volume when the system is composed solely of methane. The values of the residual specific volume of methane were obtained from the measurements of Kvalnes and Gaddy.[14] These data for pure methane are in satisfactory agreement with extrapolations of the partial volumetric behavior of methane in the methane-ethane system. The residual partial specific volumes of methane and ethane in the methane-ethane system are recorded in Table 1 as a function of pressure, temperature, and the weight fraction of the component. The experimental data[12] indicate that these gaseous mixtures do not follow the laws of ideal solutions strictly even at relatively low pressures, although the percentage deviation is small.

Some experimental information is available concerning the behavior of mixtures of methane and propane[11] in the gaseous region throughout an appreciable range of temperatures and pressures. These data are not of high accuracy, but it is believed that the partial volumetric behaviors of methane and propane derived from them are of engineering value. Although the precision of measurement was sufficient to yield reasonably-consistent residual partial specific volumes, there may be appreciable absolute uncertainties in the values. The volumetric data have been made to conform to the laws of ideal solutions at infinite attenuation. This was done because of the relatively-large uncertainties in the experimental work on this system at low pressures. The residual partial volumetric behavior of methane and propane in the methane-propane system is recorded in Table 2. The values given cover the greater part of the composition range likely to be encountered in the gases involved in production practice at pressures below 3000 pounds per square inch.

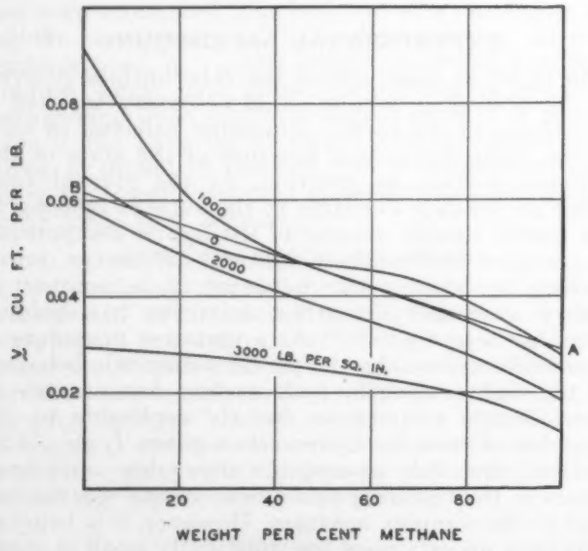

FIGURE 2

Residual Partial Specific Volumes for Methane in the Methane-Ethane System at 160° F.

From as yet unpublished data from Research Project 37 concerning the behavior of gaseous mixtures of methane and *n*butane, the residual partial volumetric behavior of these hydrocarbons has been established. It was experimentally difficult in this case to obtain high accuracy at the lower pressures, due to possible selective adsorption and to other uncertainties. For this reason the methane-*n*butane system also has been made arbitrarily to conform strictly to the laws of ideal solutions at infinite attenuation. This procedure has not caused significant divergence from the experimental data above 500 pounds per square inch, and has not involved a change in the partial volumes of either component of more than 2 percent at any state. The partial volumetric behavior of methane and of *n*butane in the gas phase of the methane-*n*butane system has been recorded in Table 3. The composition range has been restricted at the lower temperatures because of the appearance of a liquid phase at composition slightly richer in *n*butane than those recorded.

TENTATIVE APPLICATION TO COMPLEX MIXTURE

The partial specific volume of a component in a multi-component phase is a function of all the variables necessary to fix the state. Therefore, it is necessary to take into account the nature and amount of all of the other components present in order to ascertain with accuracy the partial specific volume of a component at a given pressure and temperature. At the present time there are insufficient experimental data to take all of these factors into account. Therefore, it seems desirable to employ some arbitrary means of simplifying the method of expressing the composition of the gas so that it may be treated from existing data. As was indicated in the previous section, information is available concerning the partial volumetric behavior of methane, ethane, propane, and *n*butane in binary gaseous-hydrocarbon systems containing methane. It becomes desirable, therefore, to treat the multi-component system as an equivalent quaternary system.

There are a number of arbitrary methods by which this simplification could be made. In view of the scarcity of present information to justify elaboration, a simple method will be chosen for present purposes. All components of greater molecular weight than propane will be considered, mole for mole, as *n*butane. On this basis the modified mole fraction of butane in the mixture may be evaluated by the equation:

$$\underline{n}'_4 = \sum_{k=4}^{k=n} \underline{n}_k \qquad (10)$$

If the possibility of the presence of non-hydrocarbon gases is neglected,

$$\underline{n}'_4 = 1 - \underline{n}_1 - \underline{n}_2 - \underline{n}_3 \qquad (11)$$

It should be remembered that this arbitrary simpli-

TABLE 1

Residual Partial Specific Volumes in the Gas Phase of the Methane-Ethane System

Temperature (° F.)	Pressure* (Lbs. per Sq. In.)	METHANE					ETHANE				
		Weight Percent Methane as Follows:					Weight Percent Ethane as Follows:				
		60	70	80	90	100	0	10	20	30	40
70	0	0.050†	0.0474	0.0458	0.0451	0.0449	0.1121	0.0972	0.0875	0.0831	0.0811
	250	0.0478	0.0465	0.0452	0.0446	0.0443	0.1123	0.0990	0.0911	0.0886	0.0891
	500	0.0458	0.0455	0.0445	0.0439	0.0436	0.1121	0.1004	0.0942	0.0927	0.0945
	750	0.0438	0.0445	0.0436	0.0427	0.0424	0.1112	0.1024	0.0967	0.0950	0.0974
	1,000	0.0423	0.0434	0.0424	0.0413	0.0410	0.1093	0.1027	0.0980	0.0960	0.0982
	1,500	0.0410	0.0406	0.0389	0.0377	0.0374	0.1016	0.0990	0.0948	0.0914	0.0917
	2,000	0.0384	0.0366	0.0344	0.0331	0.0329	0.0891	0.0843	0.0816	0.0744	0.0732
	2,500	0.0332	0.0309	0.0292	0.0278	0.0272	0.0752	0.0692	0.0624	0.0570	0.0528
	3,000	0.0274	0.0250	0.0232	0.0218	0.0211	0.0614	0.0537	0.0470	0.0415	0.0368
100	0	0.046	0.0431	0.0403	0.0386	0.0379	0.1069	0.0913	0.0808	0.0745	0.0706
	250	0.0434	0.0417	0.0395	0.0380	0.0373	0.1053	0.0916	0.0824	0.0779	0.0766
	500	0.0412	0.0405	0.0386	0.0371	0.0366	0.1033	0.0916	0.0838	0.0808	0.0808
	750	0.0391	0.0390	0.0375	0.0362	0.0357	0.1008	0.0910	0.0846	0.0822	0.0832
	1,000	0.0373	0.0377	0.0362	0.0348	0.0344	0.0980	0.0900	0.0846	0.0828	0.0841
	1,500	0.0344	0.0344	0.0328	0.0316	0.0313	0.0905	0.0852	0.0812	0.0788	0.0803
	2,000	0.0311	0.0304	0.0287	0.0276	0.0274	0.0800	0.0755	0.0718	0.0687	0.0681
	2,500	0.0270	0.0256	0.0243	0.0232	0.0227	0.0692	0.0632	0.0585	0.0555	0.0524
	3,000	0.0229	0.0208	0.0194	0.0183	0.0176	0.0586	0.0518	0.0462	0.0416	0.0379
130	0	0.042	0.0388	0.0354	0.0332	0.0322	0.103	0.0868	0.0748	0.0668	0.0624
	250	0.0394	0.0373	0.0346	0.0326	0.0317	0.0997	0.0860	0.0757	0.0690	0.0652
	500	0.0371	0.0359	0.0336	0.0319	0.0310	0.0964	0.0847	0.0756	0.0708	0.0678
	750	0.0349	0.0343	0.0324	0.0308	0.0300	0.0931	0.0833	0.0756	0.0718	0.0699
	1,000	0.0330	0.0327	0.0310	0.0296	0.0289	0.0897	0.0827	0.0748	0.0720	0.0712
	1,500	0.0293	0.0288	0.0276	0.0265	0.0260	0.0821	0.0750	0.0711	0.0690	0.0699
	2,000	0.0257	0.0249	0.0239	0.0232	0.0226	0.0732	0.0672	0.0634	0.0617	0.0616
	2,500	0.0222	0.0210	0.0199	0.0192	0.0187	0.0642	0.0590	0.0542	0.0514	0.0494
	3,000	0.0192	0.0172	0.0159	0.0154	0.0145	0.0558	0.0508	0.0448	0.0392	0.0351
160	0	0.037	0.0339	0.0312	0.0290	0.0278	0.1003	0.0822	0.0695	0.0607	0.0556
	250	0.0359	0.0329	0.0302	0.0284	0.0272	0.0958	0.0808	0.0695	0.0617	0.0577
	500	0.0336	0.0314	0.0292	0.0276	0.0265	0.0915	0.0790	0.0692	0.0627	0.0595
	750	0.0313	0.0300	0.0280	0.0266	0.0255	0.0872	0.0767	0.0685	0.0631	0.0609
	1,000	0.0292	0.0280	0.0266	0.0254	0.0243	0.0832	0.0744	0.0674	0.0631	0.0618
	1,500	0.0254	0.0245	0.0233	0.0225	0.0215	0.0755	0.0686	0.0633	0.0605	0.0605
	2,000	0.0217	0.0208	0.0199	0.0191	0.0185	0.0676	0.0613	0.0569	0.0544	0.0540
	2,500	0.0185	0.0174	0.0164	0.0157	0.0151	0.0600	0.0542	0.0497	0.0466	0.0448
	3,000	0.0159	0.0138	0.0128	0.0120	0.0114	0.0531	0.0472	0.0421	0.0380	0.0351
190	0	0.035	0.0316	0.0279	0.0254	0.0237	0.0983	0.0790	0.0648	0.0553	0.0498
	250	0.0326	0.0299	0.0267	0.0248	0.0233	0.0928	0.0766	0.0642	0.0558	0.0512
	500	0.0304	0.0282	0.0255	0.0238	0.0226	0.0876	0.0744	0.0637	0.0563	0.0524
	750	0.0283	0.0265	0.0242	0.0227	0.0216	0.0827	0.0716	0.0628	0.0564	0.0533
	1,000	0.0263	0.0247	0.0227	0.0213	0.0204	0.0783	0.0690	0.0615	0.0566	0.0537
	1,500	0.0224	0.0212	0.0194	0.0182	0.0177	0.0702	0.0630	0.0573	0.0536	0.0520
	2,000	0.0187	0.0178	0.0162	0.0152	0.0148	0.0628	0.0564	0.0515	0.0483	0.0468
	2,500	0.0155	0.0145	0.0131	0.0121	0.0118	0.0558	0.0501	0.0453	0.0417	0.0395
	3,000	0.0129	0.0117	0.0100	0.0089	0.0085	0.0498	0.0437	0.0386	0.0347	0.0321
220	0	0.032	0.0288	0.0251	0.0224	0.0201	0.0964	0.0758	0.0608	0.0503	0.0445
	250	0.0296	0.0268	0.0237	0.0214	0.0198	0.0902	0.0730	0.0600	0.0507	0.0455
	500	0.0275	0.0250	0.0222	0.0204	0.0191	0.0841	0.0702	0.0590	0.0509	0.0463
	750	0.0255	0.0232	0.0207	0.0192	0.0181	0.0787	0.0669	0.0577	0.0510	0.0468
	1,000	0.0235	0.0215	0.0193	0.0180	0.0170	0.0739	0.0642	0.0562	0.0503	0.0468
	1,500	0.0196	0.0178	0.0162	0.0153	0.0145	0.0656	0.0580	0.0518	0.0474	0.0450
	2,000	0.0161	0.0148	0.0132	0.0123	0.0117	0.0584	0.0518	0.0466	0.0427	0.0404
	2,500	0.0128	0.0117	0.0103	0.0094	0.0089	0.0522	0.0463	0.0409	0.0371	0.0345
	3,000	0.0103	0.0089	0.0075	0.0066	0.0059	0.0465	0.0408	0.0351	0.0310	0.0285
250	0	0.030	0.0266	0.0225	0.0193	0.0170	0.0946	0.0734	0.0574	0.0462	0.0398
	250	0.0276	0.0248	0.0209	0.0182	0.0166	0.0876	0.0700	0.0562	0.0462	0.0407
	500	0.0254	0.0227	0.0194	0.0171	0.0160	0.0812	0.0668	0.0549	0.0462	0.0413
	750	0.0234	0.0209	0.0179	0.0159	0.0150	0.0753	0.0636	0.0533	0.0457	0.0416
	1,000	0.0213	0.0191	0.0164	0.0146	0.0140	0.0701	0.0602	0.0515	0.0449	0.0414
	1,500	0.0174	0.0155	0.0134	0.0121	0.0114	0.0613	0.0536	0.0470	0.0419	0.0392
	2,000	0.0137	0.0124	0.0105	0.0092	0.0087	0.0541	0.0472	0.0415	0.0373	0.0350
	2,500	0.0105	0.0095	0.0078	0.0066	0.0061	0.0479	0.0414	0.0362	0.0320	0.0298
	3,000	0.0079	0.0067	0.0052	0.0039	0.0034	0.0427	0.0363	0.0311	0.0267	0.0244

* All pressures are in pounds per square inch, absolute.
† Residual partial specific volume, cubic feet per pound.

fication of the composition of the system inevitably introduces uncertainties in the predictions of volume. As more experimental measurements accumulate, it will be possible to employ equivalent systems of five or more components, and thus approach more nearly to the actual case.

The experimental information presented in an earlier section of this paper related to the residual partial specific volume, i. e., the residual partial volume per unit weight of component. Therefore, it is necessary to employ the weight fraction, as determined from the modified composition, rather than the mole fraction in the estimation of the specific volume of a complex gaseous mixture by the methods proposed in this paper.

The experimental information available concerning the partial volumetric behavior of methane permits the estimation of the effect of pressure, temperature, the concentration of methane and, roughly, of the nature of the other components present. It has been assumed that the residual partial specific volume of methane at a particular pressure, temperature, and weight fraction of methane is equivalent to the weighted mean of the residual partial specific volumes of methane in each of the three binary hydrocarbon systems at the same pressure, temperature, and weight fraction of methane. In obtaining this mean, the weight given to the value from a particular binary system is in direct proportion to the concentration of the heavier component of the binary system in question. On the basis of this assumption, the residual partial specific volume of methane may be established from the following expression:

$$\overline{V}_1 = \frac{(\overline{V}_1)_{1:2}n_2 + (\overline{V}_1)_{1:3}n_3 + (\overline{V}_1)_{1:4}n_4}{1-n_1} \qquad (12)$$

It should be realized that difficulty in the direct ap-

TABLE 2

Residual Partial Specific Volumes in the Gas Phase of the Methane-Propane System

Temperature (Deg. F.)	Pressure (Lbs. per Sq. In.)	METHANE					PROPANE				
		Weight Percent Methane as Follows:					Weight Percent Propane as Follows:				
		60	70	80	90	100	0	10	20	30	40
70	0	0.045*	0.045	0.045	0.045	0.0449	0.131	0.131	0.131	0.131	0.131
	250	0.041	0.042	0.044	0.044	0.0443	0.118	0.122	0.125	0.128	0.131
	500	0.039	0.040	0.042	0.043	0.0436	0.107	0.113	0.118	0.123	0.127
	750	0.037	0.039	0.041	0.042	0.0424	0.099	0.105	0.111	0.116	0.121
	1,000	0.035	0.037	0.039	0.041	0.0410	0.091	0.098	0.104	0.109	0.113
	1,500	0.032	0.034	0.036	0.037	0.0374	0.075	0.083	0.089	0.094	0.098
	2,000	0.029	0.030	0.031	0.032	0.0329	0.059	0.067	0.072	0.076	0.077
	2,500	0.027	0.026	0.026	0.027	0.0272	0.049	0.051	0.052	0.054	0.055
	3,000	0.024	0.022	0.021	0.021	0.0211	0.041	0.040	0.038	0.035	0.032
100	0	0.038	0.038	0.038	0.038	0.0379	0.116	0.116	0.116	0.116	0.116
	250	0.035	0.036	0.037	0.037	0.0373	0.103	0.106	0.110	0.114	0.119
	500	0.032	0.034	0.036	0.036	0.0366	0.093	0.097	0.103	0.111	0.118
	750	0.029	0.032	0.034	0.035	0.0357	0.082	0.089	0.097	0.106	0.116
	1,000	0.027	0.031	0.033	0.034	0.0344	0.074	0.081	0.089	0.099	0.111
	1,500	0.023	0.027	0.030	0.031	0.0313	0.061	0.067	0.075	0.084	0.094
	2,000	0.020	0.021	0.026	0.027	0.0274	0.050	0.057	0.061	0.066	0.067
	2,500	0.018	0.023	0.022	0.023	0.0227	0.041	0.045	0.044	0.051	0.052
	3,000	0.018	0.017	0.017	0.018	0.0176	0.032	0.033	0.034	0.034	0.032
130	0	0.032	0.032	0.032	0.032	0.0322	0.104	0.104	0.104	0.104	0.104
	250	0.030	0.031	0.031	0.031	0.0317	0.091	0.093	0.095	0.098	0.101
	500	0.027	0.029	0.030	0.030	0.0310	0.081	0.084	0.088	0.093	0.098
	750	0.025	0.028	0.029	0.029	0.0300	0.072	0.076	0.081	0.087	0.094
	1,000	0.023	0.026	0.027.	0.028	0.0289	0.065	0.070	0.075	0.082	0.090
	1,500	0.019	0.023	0.025	0.026	0.0260	0.053	0.058	0.064	0.071	0.078
	2,000	0.016	0.019	0.021	0.022	0.0226	0.043	0.048	0.054	0.059	0.064
	2,500	0.014	0.015	0.018	0.019	0.0187	0.034	0.039	0.043	0.046	0.048
	3,000	0.014	0.014	0.014	0.014	0.0145	0.027	0.029	0.031	0.032	0.033
160	0	0.028	0.028	0.028	0.028	0.0278	0.094	0.094	0.094	0.094	0.094
	250	0.026	0.027	0.027	0.027	0.0272	0.084	0.083	0.084	0.085	0.087
	500	0.024	0.025	0.026	0.026	0.0265	0.075	0.076	0.077	0.079	0.083
	750	0.022	0.024	0.025	0.025	0.0255	0.068	0.070	0.072	0.075	0.076
	1,000	0.020	0.022	0.023	0.024	0.0243	0.062	0.064	0.066	0.069	0.074
	1,500	0.017	0.019	0.021	0.021	0.0215	0.050	0.053	0.057	0.061	0.066
	2,000	0.014	0.017	0.018	0.018	0.0185	0.041	0.045	0.049	0.053	0.057
	2,500	0.012	0.014	0.015	0.015	0.0151	0.034	0.037	0.040	0.043	0.045
	3,000	0.010	0.011	0.011	0.011	0.0114	0.027	0.029	0.031	0.032	0.033
190	0	0.024	0.024	0.024	0.024	0.0237	0.085	0.085	0.085	0.085	0.085
	250	0.022	0.023	0.023	0.023	0.0233	0.078	0.077	0.076	0.077	0.079
	500	0.021	0.022	0.023	0.023	0.0226	0.072	0.070	0.070	0.071	0.074
	750	0.020	0.021	0.022	0.022	0.0216	0.067	0.065	0.065	0.066	0.070
	1,000	0.018	0.020	0.020	0.020	0.0204	0.061	0.060	0.060	0.062	0.066
	1,500	0.016	0.017	0.018	0.018	0.0177	0.050	0.050	0.052	0.054	0.058
	2,000	0.013	0.014	0.015	0.015	0.0148	0.040	0.042	0.044	0.046	0.049
	2,500	0.011	0.011	0.011	0.012	0.0118	0.033	0.035	0.037	0.038	0.040
	3,000	0.009	0.009	0.008	0.008	0.0085	0.029	0.030	0.031	0.031	0.031

* Residual partial specific volume, cubic feet per pound.

plication of equation (12) arises when the concentration of methane in the multi-component system is sufficiently low to permit the existence of two phases at this composition in one or more of the binary systems considered. Under these circumstances there are at least two approaches possible. The residual partial specific volume may be extrapolated from the single-phase region of the binary system in question, or the influence of these heavier components upon the partial volumetric behavior of methane may be neglected. It should be realized that the uncertainty in the estimation of the partial volumetric behavior of methane concerns only the difference between the actual behavior and the perfect gas behavior, and is not involved proportionately in the estimation of the partial volume directly.

The residual partial volumetric behavior of ethane in a complex mixture for the present must be taken as equal to that for ethane in the methane-ethane system at the same pressure, temperature, and weight fraction of ethane. This procedure assumes, in effect, that the heavier components have the same influence upon the partial specific volume of ethane as does methane. The behavior of propane and *n*butane also may be taken to be equal to that of these components in the methane-propane and methane-*n*butane systems, respectively.

This procedure permits the direct utilization of the tabulated residual partial specific volumes of methane, ethane, propane, and *n*butane in the prediction of the volumetric behavior of multi-component gaseous-hydrocarbon mixtures. If the non-condensible gases such as hydrogen, nitrogen, oxygen and, possibly, carbon dioxide are neglected insofar as deviations from the perfect gas laws are concerned, the specific volume is related to the residual partial volume in the following way:

$$V = \frac{10.732\ T}{M_a P} - \bar{V}_1 n_1 - \bar{V}_2 n_2 - \bar{V}_3 n_3 - \bar{V}_4 n_4 \qquad (13)$$

The first term of this expression would represent the specific volume of the natural gas if it followed the perfect gas laws, whereas the succeeding terms are the deviations of the partial specific volumes of each of the components from this idealized behavior. If desired, equation (13) may be combined with equation (12) to yield a somewhat more directly-applicable relationship:

$$V = \frac{10.732\ T}{M_a P} - \left(\frac{n_1}{1-n_1}\right)\left[(\bar{V}_1)_{1;2} n_2 + (\bar{V}_1)_{1;3} n_3 + (\bar{V}_1)_{1;4} n_4\right] - \bar{V}_2 n_2 - \bar{V}_3 n_3 - \bar{V}_4 n_4 \qquad (14)$$

It is seen that equation (14) does not involve any quantity which cannot be estimated from information recorded in Tables 1 to 3, or which is not given by the composition of the gas. In this method of correlation, because the composition exerts a direct influ-

TABLE 3

Residual Partial Specific Volumes in the Gas Phase of the Methane-*n*Butane System

Temperature (Deg. F.)	Pressure (Lbs. per Sq. In.)	METHANE					*n*BUTANE				
		Weight Percent Methane as Follows:					Weight Percent *n*Butane as Follows:				
		60	70	80	90	100	0	10	20	30	40
70	0	0.0449*	0.0449	0.0449	0.0449	0.0449	0.1804	0.1804	0.1804	0.1804	0.1804
	250	0.0307	0.0367	0.0405	0.0426	0.0443	0.1378	0.1426	0.1452	0.1562	0.1699
	500	.....	.....	0.0418	0.0428	0.0436	0.1226	0.1305	0.1278	.....	.....
	750	.....	.....	0.0422	0.0420	0.0424	0.1126	0.1196	0.1156	.....	.....
	1,000	.....	.....	0.0414	0.0412	0.0410	0.1045	0.1100	0.1056	.....	.....
	1,500	.....	.....	0.0382	0.0376	0.0374	0.0914	0.0919	0.0871	.....	.....
	2,000	.....	.....	0.0336	0.0327	0.0329	0.0787	0.0753	0.0717	.....	.....
	2,500	.....	.....	0.0284	0.0271	0.0272	0.0643	0.0605	0.0570	.....	.....
	3,000	.....	.....	0.0226	0.0212	0.0211	0.0503	0.0473	0.0435	.....	.....
100	0	0.0379	0.0379	0.0379	0.0379	0.0379	0.1719	0.1719	0.1719	0.1719	0.1719
	250	0.0251	0.0319	0.0355	0.0365	0.0373	0.1316	0.1340	0.1387	0.1466	0.1613
	500	.....	0.0344	0.0362	0.0366	0.0366	0.1201	0.1208	0.1230	0.1246	.....
	750	.....	0.0358	0.0362	0.0363	0.0357	0.1104	0.1096	0.1096	0.1095	.....
	1,000	.....	0.0357	0.0357	0.0352	0.0344	0.1028	0.1000	0.0985	0.0975	.....
	1,500	.....	0.0335	0.0328	0.0318	0.0313	0.0916	0.0855	0.0808	0.0785	.....
	2,000	.....	0.0298	0.0287	0.0275	0.0274	0.0785	0.0704	0.0657	0.0624	.....
	2,500	.....	0.0252	0.0239	0.0228	0.0227	0.0626	0.0574	0.0532	0.0492	.....
	3,000	.....	0.0203	0.0187	0.0179	0.0176	0.0464	0.0439	0.0416	0.0366	.....
130	0	0.0322	0.0322	0.0322	0.0322	0.0322	0.1630	0.1630	0.1630	0.1630	0.1630
	250	0.0218	0.0281	0.0306	0.0314	0.0317	0.1302	0.1295	0.1333	0.1397	0.1521
	500	0.0213	0.0289	0.0310	0.0310	0.0310	0.1182	0.1140	0.1129	0.1165	0.1323
	750	0.0220	0.0307	0.0309	0.0304	0.0300	0.1092	0.1030	0.0994	0.1010	0.1136
	1,000	0.0231	0.0305	0.0303	0.0295	0.0289	0.1018	0.0940	0.0889	0.0891	0.0993
	1,500	0.0241	0.0282	0.0280	0.0269	0.0260	0.0879	0.0781	0.0731	0.0719	0.0779
	2,000	0.0231	0.0247	0.0245	0.0232	0.0226	0.0747	0.0646	0.0596	0.0578	0.0616
	2,500	0.0221	0.0206	0.0204	0.0190	0.0187	0.0593	0.0525	0.0485	0.0468	0.0474
	3,000	0.0180	0.0159	0.0152	0.0147	0.0145	0.0431	0.0408	0.0393	0.0367	0.0334
160	0	0.0278	0.0278	0.0278	0.0278	0.0278	0.1508	0.1508	0.1508	0.1508	0.1508
	250	0.0209	0.0243	0.0260	0.0269	0.0272	0.1256	0.1266	0.1293	0.1338	0.1428
	500	0.0189	0.0257	0.0268	0.0264	0.0265	0.1140	0.1099	0.1070	0.1091	0.1224
	750	0.0183	0.0264	0.0265	0.0258	0.0255	0.1010	0.0970	0.0919	0.0930	0.1049
	1,000	0.0184	0.0260	0.0257	0.0248	0.0243	0.0927	0.0863	0.0809	0.0814	0.0909
	1,500	0.0186	0.0235	0.0235	0.0222	0.0215	0.0809	0.0708	0.0656	0.0652	0.0726
	2,000	0.0169	0.0201	0.0206	0.0192	0.0185	0.0688	0.0589	0.0536	0.0530	0.0598
	2,500	0.0148	0.0163	0.0167	0.0158	0.0151	0.0552	0.0482	0.0440	0.0436	0.0474
	3,000	0.0129	0.0123	0.0120	0.0117	0.0114	0.0403	0.0380	0.0368	0.0356	0.0340
190	0	0.0237	0.0237	0.0237	0.0237	0.0237	0.1452	0.1452	0.1452	0.1452	0.1452
	250	0.0197	0.0215	0.0224	0.0229	0.0233	0.1254	0.1253	0.1258	0.1289	0.1324
	500	0.0175	0.0220	0.0228	0.0223	0.0226	0.1094	0.1052	0.1022	0.1042	0.1131
	750	0.0160	0.0221	0.0229	0.0216	0.0217	0.0965	0.0903	0.0854	0.0867	0.0946
	1,000	0.0155	0.0215	0.0221	0.0207	0.0204	0.0857	0.0794	0.0737	0.0743	0.0821
	1,500	0.0146	0.0191	0.0198	0.0183	0.0177	0.0714	0.0642	0.0587	0.0587	0.0662
	2,000	0.0122	0.0161	0.0169	0.0156	0.0148	0.0592	0.0526	0.0481	0.0479	0.0559
	2,500	0.0101	0.0128	0.0134	0.0125	0.0118	0.0484	0.0437	0.0400	0.0402	0.0451
	3,000	0.0088	0.0092	0.0092	0.0091	0.0085	0.0389	0.0355	0.0345	0.0340	0.0341
220	0	0.0201	0.0201	0.0201	0.0201	0.0201	0.1350	0.1350	0.1350	0.1350	0.1350
	250	0.0184	0.0192	0.0197	0.0196	0.0198	0.1233	0.1224	0.1256	0.1256	0.1255
	500	0.0167	0.0190	0.0193	0.0189	0.0191	0.1083	0.1014	0.0988	0.0988	0.1042
	750	0.0152	0.0190	0.0187	0.0181	0.0181	0.0913	0.0846	0.0797	0.0797	0.0889
	1,000	0.0138	0.0185	0.0180	0.0172	0.0170	0.0784	0.0721	0.0677	0.0677	0.0731
	1,500	0.0110	0.0159	0.0162	0.0150	0.0145	0.0638	0.0572	0.0524	0.0524	0.0589
	2,000	0.0085	0.0128	0.0137	0.0126	0.0117	0.0545	0.0477	0.0429	0.0429	0.0512
	2,500	0.0064	0.0096	0.0104	0.0097	0.0089	0.0469	0.0402	0.0368	0.0368	0.0430
	3,000	0.0053	0.0062	0.0065	0.0064	0.0059	0.0354	0.0331	0.0324	0.0324	0.0331
250	0	0.0170	0.0170	0.0170	0.0170	0.0170	0.1344	0.1344	0.1344	0.1344	0.1344
	250	0.0178	0.0160	0.0162	0.0162	0.0166	0.1226	0.1233	0.1240	0.1240	0.1183
	500	0.0151	0.0157	0.0160	0.0154	0.0160	0.1014	0.0997	0.0934	0.0934	0.0930
	750	0.0140	0.0160	0.0156	0.0146	0.0150	0.0830	0.0787	0.0733	0.0733	0.0766
	1,000	0.0121	0.0156	0.0149	0.0136	0.0140	0.0714	0.0660	0.0614	0.0614	0.0646
	1,500	0.0085	0.0131	0.0131	0.0117	0.0114	0.0573	0.0514	0.0462	0.0462	0.0514
	2,000	0.0055	0.0098	0.0107	0.0097	0.0087	0.0500	0.0432	0.0384	0.0384	0.0460
	2,500	0.0034	0.0068	0.0077	0.0072	0.0061	0.0429	0.0367	0.0334	0.0334	0.0398
	3,000	0.0026	0.0036	0.0042	0.0040	0.0034	0.0332	0.0306	0.0307	0.0307	0.0315

* Residual partial specific volume, cubic feet per pound.

ence upon the specific volume evaluated, any error in the analysis of the gas is reflected directly in the predicted specific volumes.

ILLUSTRATIVE APPLICATIONS

Experimental information concerning the volumetric behavior of multi-component hydrocarbon gases affords a means of ascertaining the accuracy of prediction which may be made with these methods in their present incomplete state. Experimental measurements upon four different samples of natural gas here are utilized in this comparison. The analyses of these gases are given in Table 4. Table 5 presents an illustrative numerical example of the application of equation (14) for each gas at a single state. In the case of gas *C* it was necessary to take into account the presence of a significant quantity of carbon dioxide, nitrogen, and oxygen. These non-hydrocarbon components of gas *C* were treated as though they followed the laws of ideal solution and were perfect gases. In computing the residual partial specific volumes of the hydrocarbon components, the presence of these non-hydrocarbon gases was neglected. This necessitated a modification of the residual specific volume computed for the hydrocarbon components

TABLE 4

Analyses of Gases
(Expressed as Mole Fraction)

Component	Gas *A*[21]	Gas *B* *	Gas *C*[22]	Gas *D*[23]
Carbon dioxide	0.000	0.0020	0.006	.....
Nitrogen and Oxygen	0.000	0.000	0.015	.....
Methane	0.8319	0.8652	0.8778	0.9500
Ethane	0.0848	0.0575	0.0382	0.0300
Propane	0.0437	0.0414	0.0336	0.0200
*Iso*butane	0.0076	0.0085	0.0074	.....
*n*Butane	0.0168	0.0161	0.0126	.....
*Iso*pentane	0.0057	0.0083	0.0038	.....
*n*Pentane	0.0032	0.0010	0.0026	.....
Hexanes	0.0063	.....	0.0030	.....

* Unpublished data from API Research Project 37.

TABLE 5

Illustrative Calculations Utilizing Equation (14)

Equation:

$$V=\frac{10.732\,T}{M_a P}-\left[\frac{n_1}{1-n_1}\right]\left[(\bar{Y}_1)_{1:2}n_2+(\bar{Y}_1)_{1:3}n_3+(\bar{Y}_1)_{1:4}n_4\right]-\bar{Y}_2n_2-\bar{Y}_3n_3-\bar{Y}_4n_4$$

Gas *A* at 160 deg. F. and 2,000 lb. per sq. in., absolute

$$V=\frac{(10.732)\,(619.7)}{(20.43)\,(2{,}000)}-\left[\frac{0.6632}{0.3368}\right]\left[(0.0215)\,(0.1267)+(0.0158)\,(0.0958)+(0.0185)\,(0.1144)\right]$$
$$-(0.0599)\,(0.1267)-(0.0447)\,(0.0958)-(0.0589)\,(0.1144)=0.1317 \text{ cu. ft. per lb.}$$

Gas *B* at 130 deg. F. and 1,000 lb. per sq. in., absolute

$$V=\frac{(10.732)\,(589.7)}{(19.61)\,(1{,}000)}-\left[\frac{0.7154}{0.2846}\right]\left[(0.0320)\,(0.0891)+(0.0260)\,(0.0941)+(0.0305)\,(0.1015)\right]$$
$$-(0.0823)\,(0.0891)-(0.0693)\,(0.0941)-(0.0940)\,(0.1015)=0.2782 \text{ cu. ft. per lb.}$$

Gas *C* at 160 deg. F. and 2,000 lb. per sq. in., absolute

$$V=\frac{(10.732)\,(619.7)}{(19.31)\,(2{,}000)}-(0.9632)^{*}\left\{\left[\frac{0.7645}{0.2355}\right]\left[(0.0204)\,(0.0624)+(0.0174)\,(0.0805)+(0.0203)\,(0.0928)\right]\right.$$
$$\left.-(0.0634)\,(0.0624)-(0.0440)\,(0.0805)-(0.0589)\,(0.0928)\right\}=0.1455 \text{ cu. ft. per lb.}$$

Gas *D* at 80 deg. F. and 2,000 lb. per sq. in., absolute

$$V=\frac{(10.732)\,(539.7)}{(17.02)\,(2{,}000)}-\left[\frac{0.895}{0.105}\right]\left[(0.0313)\,(0.053)+(0.030)\,(0.052)\right]$$
$$-(0.0835)\,(0.053)-(0.060)\,(0.052)=0.1352 \text{ cu. ft. per lb.}$$

* Total weight fraction of hydrocarbons. In this case all *n*-values in the equation are based upon hydrocarbons only.

which is not involved in the computations for the other gases. This treatment of non-hydrocarbon gases is arbitrary, but probably does not introduce significant uncertainties as long as the gases involved do not contain large quantities of these components. The calculation represented by equation (14) is somewhat longer than would be desired. However, it is believed that it represents as great a simplification of a complex problem as could be made without introducing uncertainties of engineering significance, even though a much more complete experimental background were employed than is at present available.

Table 6 offers a comparison of the experimental and calculated specific volumes of the four gases employed.

In all cases the calculated values are somewhat lower than the experimentally-measured specific volumes at the highest pressures recorded. This probably results from the use of the residual partial specific volume of *n*butane to represent the partial volumetric behavior of the heavier components. At the higher pressures there appears to be a tendency for the residual partial specific volumes of the hydrocarbon components to decrease with an increase in molecular weight, whereas the reverse tendency exists at the lower pressures. These trends would indicate that the predictions of specific volume would be too large at the low pressures, and too small at the higher pressures, as a result of the use of the values for *n*butane as representative of the heavier components. These trends correspond in general with the discrepancies given in Table 6.

In all cases except for gas *C*, the agreement is considered satisfactory at pressures up to 2000 pounds per square inch. Deviations as large as 2.9 percent are involved at the lower pressures for gas *C*. The experimental method used to determine the specific volume of this gas was such that uncertainties in the analysis would tend to cause more important discrepancies between experimental and predicted values. This case was complicated also by the presence of significant quantities of non-hydrocarbon gases.

The rapidly-increasing uncertainty involved in the predictions at pressures above 2000 pounds per square

TABLE 6

Comparison of Experimental and Calculated Specific Volumes

Temperarure (Deg. F.)	Pressure (Lbs. per Sq. In.)	Specific Volume (Cu. Ft., per Lb.)		Error Percent
		Experimental	Calculated	
GAS *A*				
100	500	0.5300[21]	0.5335	+0.7
	1,000	0.2412	0.2414	+0.1
	2,000	0.1064	0.1065	+0.1
	3,000	0.0736	0.700	—4.9
160	500	0.6063	0.6037	—0.4
	1,000	0.2856	0.2843	—0.5
	2,000	0.1326	0.1317	—0.7
	3,000	0.0892	0.0872	—2.2
220	500	0.6803	0.6742	—0.9
	1,000	0.3282	0.3232	—1.5
	2,000	0.1569	0.1547	—1.4
	3,000	0.1051	0.1026	—2.4
GAS *B*				
70	500	0.5145*	0.5181	+0.7
	1,000	0.2292	0.2329	+1.6
130	500	0.5960	0.5960	0.0
	1,000	0.2779	0.2782	+0.1
GAS *C*				
160	500	0.6355[22]	0.6482	+2.0
	1,000	0.3045	0.3083	+1.2
	2,000	0.1480	0.1454	—1.8
	3,000	0.1022	0.0973	—4.7
220	500	0.7004	0.7206	+2.9
	1,000	0.3453	0.3489	+1.0
	2,000	0.1663	0.1682	+1.1
	3,000	0.1120	0.1091	—2.6
GAS *D*				
80	500	0.6260[23]	0.6325	+1.0
	1,000	0.2919	0.2962	+1.5
	2,000	0.1340	0.1351	+0.8
	3,000	0.0907	0.0902	—0.6

* Unpublished data from API Research Project 37.

inch indicates that more detailed information than at present is available will be necessary in order to predict volumetric behavior with accuracy in this region. However, it is believed that the agreement, even on the present basis, is sufficiently good in most cases that the method of prediction may be of engineering value. As more information accumulates, it will be possible to take into account pertinent factors which were omitted in this tentative approach. The method is such that it permits the utilization of new information as it becomes available.

SUMMARY

A method has been proposed for the prediction of the specific volume of complex gaseous-hydrocarbon mixtures. The procedure to be followed in using this method may be summarized in the following steps:

1. The analysis of the gas, which commonly is expressed as the mole fraction of each of the components present, first is modified to yield a corresponding quaternary analysis by application of equation (10) or (11).
2. The corresponding quaternary analysis is reexpressed in terms of weight fractions instead of mole fractions.
3. The residual partial specific volumes of methane, ethane, propane, and *n*butane for the prevailing pressure, temperature, and weight fraction of the component in question are interpolated from the information recorded in Tables 1 to 4, inclusive. In general, simple linear interpolation with respect to pressure, temperature, and composition is adequate for this purpose. The value used for metane is taken as a weighted mean of the values obtained for the binary systems involving methane with each of the other components of the modified analysis in accordance with equation (12).
4. The average molal weight M_a of the gas is computed from the original analysis.
5. The specific volume is calculated directly by substitution of the appropriate values in equation (14).

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NOMENCLATURE

b	Specific gas constant; $\frac{R}{M} = \frac{10.732}{M}$ (lb. per sq. in.) (cu. ft. per lb.) per deg. F., absolute.
M	Molal weight, pounds.
M_a	Average molal weight, obtained from actual analysis, pounds.
m_k	Weight of component *k*, pounds.
$\underline{n}$	Mole fraction.
$\underline{n}'$	Modified mole fraction.
n	Weight fraction in modified analysis.
P	Pressure, pounds per square inch, absolute.
T	Temperature, deg. F., absolute.
$\underline{V}$	Total volume of system, cubic feet.
$\overline{V}$	Specific volume, cubic feet per pound.
V_R	Reference specific volume, cubic feet per pound.
$\underline{V}$	Residual specific volume, cubic feet per pound.
$\overline{V}$	Partial specific volume, cubic feet per pound.
$\overline{\underline{V}}$	Residual partial specific volume, cubic feet per pound.
$(\overline{\underline{V}}_1)_{1:2}$	Residual partial specific volume of methane in the methane-ethane system, cubic feet per pound.
Subscripts 1, 2, 3, 4	refer to methane, ethane, propane, and *n*butane, respectively.
Subscript n	refers to component *n* in an *n*-component system.
Subscript k	refers to any component *k*.
Subscript i	refers to all components except component *k*.

BIBLIOGRAPHY

[1] Beattie, *J. Am. Chem. Soc.* **51**, 19 (1929).
[2] Keyes and Burks, *ibid.* **49**, 1403 (1927).
[3] Masson and Dolley, *Proc. Roy. Soc.* **103A**, 524 (1923).
[4] Gilliland, *Ind. Eng. Chem.* **28**, 212 (1936).
[5] Kay, *ibid.* **28**, 1014 (1936).
[6] Lewis, *Proc. Am. Acad. Arts and Sci.* **43**, 273 (1907).
[7] Sage, Hicks, and Lacey, *Drilling and Production Practice, 1938*, 402.
[8] Lewis and Randall, *Thermodynamics*, 42, McGraw-Hill Book Co., New York (1923).
[9] Sage and Lacey, *Ind. Eng. Chem.* **31**, 000 (1940) (in publication).
[10] Roozeboom, *Die Heterogenen Gleichgewichte* **[II-1]** 288, Braunschweig (1904).
[11] Sage, Lacey, and Schaafsma, *Ind. Eng. Chem.* **26**, 214 (1934).
[12] Sage and Lacey, *Ind. Eng. Chem.* **31**, 000 (1940) (in publication).
[13] Sage, Hicks, and Lacey, unpublished data from API Research Project 37.
[14] Kvalnes and Gaddy, *J. Am. Chem. Soc.* **53**, 398 (1931).
[15] Beattie, Hadlock, and Poffenberger, *J. Chemical Physics* **3**, 93 (1935).
[16] Sage, Webster, and Lacey, *Ind. Eng. Chem.* **29**, 658 (1937).
[17] Beattie, Kay, and Kaminsky, *J. Am. Chem. Soc.* **59**, 1509 (1937).
[18] Nellis, Master's Thesis, California Institute of Technology (1938).
[19] Beattie, Simard, and Gouq-Jen Su, *J. Am. Chem. Soc.* **61**, 26 (1939).
[20] Sage, Webster, and Lacey, *Ind. Eng. Chem.* **29**, 1188 (1937).
[21] Sage and Lacey, *Drilling and Production Practice, 1936*, 158.
[22] Sage and Lacey, *Ind. Eng. Chem.* **28**, 249 (1936).
[23] Carter and Webber, *Refiner and Natural Gasoline Mfr.* **18** [5] 206 (1939).

Catalytic Desulfurization *to Improve* Aviation Blending Naphthas

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EXPERIMENTAL investigation has shown that the tetraethyl-lead response of aviation gasolines consisting of blends of *iso*octane base and straight-run naphtha either of refinery or natural-gasoline origin may be improved markedly by removal of the sulfur compounds from the naphtha. Practically complete desulfurization has been obtained by treatment of the naphtha vapors over bauxite catalyst at temperatures of 700 to 750° F.

Inasmuch as the desulfurized blends have greater lead response, the minimum percentage of *iso*-octane required in high-octane gasoline may be reduced appreciably. It is possible, therefore, to increase the production of high-octane gasoline without a corresponding increase in *iso*octane base. If desired, the hydrocarbon composition of the blend may be left unchanged, and a higher-octane gasoline be produced as a result of the improved lead response.

In the case of Hobbs pentane-free natural gasoline, the production of high-octane blended and ethylized aviation gasoline for a given amount of *iso*octane was increased as follows:

92 octane number with 0.5 ml. TEL†—19.7 percent
100 octane number with 3.0 ml. TEL —27.7 percent
87 octane number with 1.0 ml. TEL —52.2 percent

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

SOME very notable advances have been made in aviation gasoline within the last few years, the greatest single improvement having come with the manufacture of *iso*octane on a commercial scale. In service these high-octane gasolines have shown such marked superiority over the lower-octane fuels that a great deal of emphasis is being placed today on means of still further improvement.

Because *iso*octane does not possess the proper vapor-pressure or distillation characteristics of a finished gasoline, it must be considered merely as a blending stock. This means, of course, that attention must be focused on the naphthas which are blended with the *iso*octane. For example, in the manufacture of 100-octane ethylized gasoline, it is common practice for the finished blend to contain from 35 to 60 percent commercial *iso*octane—the remainder being refinery straight-run gasoline. In some instances, however, as much as 25 percent of *iso*pentane is used, the aviation blending naphtha in such cases usually being depentanized or fractionated to a comparatively-high initial boiling point. The straight-run gasolines may range from selected natural gasolines to high-octane naphthas of relatively-high boiling points. In most instances the maximum permissible tetraethyl lead (TEL) is 3.0 ml. per gallon, although still higher maxima sometimes are permitted. To simplify the present discussion, the maximum TEL content of 3.0 ml. has been selected.

In the manufacture of aviation gasolines of less than 100 octane number, the anti-knock characteristics of the blending naphthas are likewise of importance. Two typical examples have been selected for this study, viz.: 1, 92-octane gasoline, with a maximum of 0.5 ml. TEL per gallon; and, 2, 87-octane gasoline, with a maximum of 1.0 ml. per gallon. In both instances it has been assumed that commercial *iso*octane and *iso*pentane would be blended with a straight-run or natural gasoline.

EFFECT OF SULFUR ON LEAD RESPONSE

Schulze and Buell in an article published in 1935 showed how sulfur compounds present in motor fuels affect the lead responsiveness of such fuels.[1] Other workers have confirmed these results.[2,3] Of the various classes of sulfur compounds in petroleum oils, the most common are hydrogen sulfide, elementary sulfur, mercaptans, aliphatic and aromatic monosulfides and disulfides, and cyclic sulfur compounds such as the thiophenes and the "thiophanes." Occasionally there also may be found alkyl polysulfides, resulting from certain sweetening processes; and sometimes there may be traces of sulfones and sulfoxides. As chemical treatment usually is employed to remove the corrosive compounds and the mercaptans are converted to disulfides in some sort of sweetening process, we are interested primarily in the effects produced by the monosulfides, disulfides, and cyclic sulfur compounds. Figure 1, reproduced from the previously-mentioned paper,[1] shows the behavior of certain members of each of these classes of sulfur compounds. It should be noted especially that the deleterious effect of sulfur is greatest at low concentrations; this means that the removal of even small amounts of sulfur from the aviation blending stocks will produce sizeable increases in lead response.

CATALYTIC DESULFURIZATION OF COMPONENTS OF 100-OCTANE GASOLINE

Most of the commercial *iso*octane produced has a very low sulfur content, because the methods of manufacture include desulfurization of the feed stocks. Therefore, improvement in the TEL response of the commercial *iso*octane, if needed, is attained by methods other than those here proposed. *Iso*pentane is produced

† Tetraethyl lead.

practically free of sulfur and, in addition, has a tremendous susceptibility to TEL. Consequently, improvement in lead response by reduction of the sulfur content is limited largely to the aviation naphthas used in blending. It is on these latter stocks that catalytic desulfurization shows such excellent results.

In the catalytic treatment, the hydrocarbon vapors are contacted at temperatures in the range of 700 to 750 °F. with bauxite catalyst, whereby the sulfur compounds are decomposed into hydrogen sulfide. Inasmuch as complete removal of mercaptans, monosulfides, and disulfides can be obtained in this manner, and as very little or no cyclic sulfur is present in these low-boiling gasolines, it is possible to produce practically sulfur-free stocks.

Numerous natural gasolines and straight-run naphthas have been subjected to appraisal. To indicate the results obtainable, data on four stocks are presented herewith. The characteristics of the four stocks are summarized briefly in the following tabulation:

Description	Borger "Butane-free" Natural Gasoline	Borger "Pentane-free" Natural Gasoline	Hobbs "Pentane-free" Natural Gasoline	New Mexico Straight-run Gasoline
Reid vapor pressure, lb. per sq. in.	12.0	6.4	5.2	11.2
ASTM Distillation, in °F.:				
10-percent point	103	142	161	121
50-percent point	122	164	174	150
90-percent point	201	226	229	180
Sulfur, percent	0.037	0.057	0.096	0.013
Octane No. (unleaded)	67.2	59.2	65.6	76.0

The stocks represented by the tabulation were selected as examples to cover high, medium, and low sulfur contents, and to include a wide range of octane numbers of the untreated gasolines. In general, the boiling range of the gasoline has no relationship to the improvements in lead susceptibility as attained by bauxite desulfurization.

Table 1 gives the octane-number and lead-response data on Borger 12-pound natural gasoline desulfurized to different levels.

It should be noted that there is a very appreciable difference in lead response between the gasolines of 0.008 and 0.004 percent sulfur content. A definite but smaller improvement is apparent in further reducing the sulfur to 0.002 percent. A similar effect on the original octane numbers may be noted. This wide difference in lead response between gasolines with only a few thousandths percent difference in sulfur content as the sulfur content approaches zero is greater than most people have suspected. The increasing difference as greater amounts of lead are added is especially significant with respect to aviation fuels. A graphical representation of these effects is given in Figure 2.

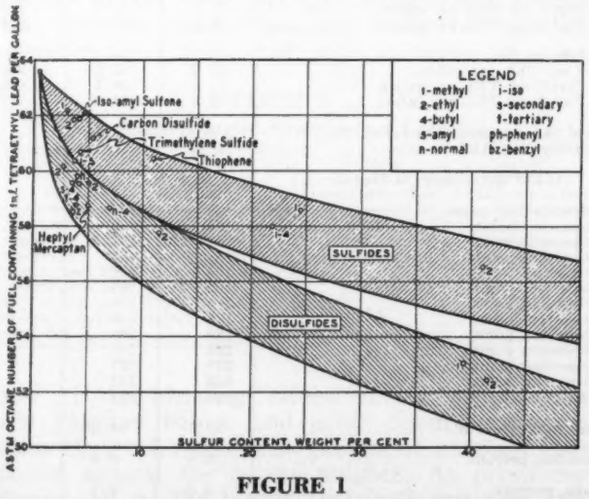

FIGURE 1

Effect of Various Sulfur Compounds on Lead Susceptibility of Reference Fuel

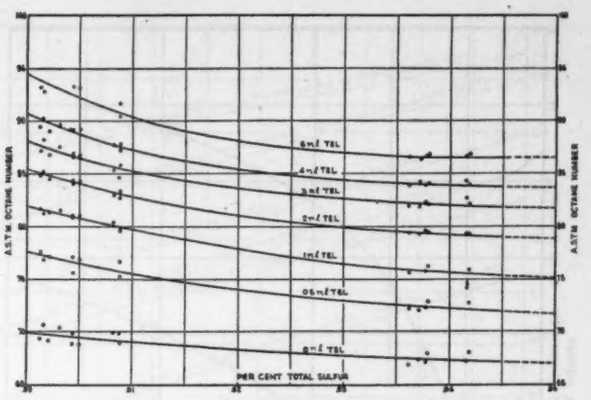

FIGURE 2

Effect of Sulfur Content on Tetraethyl-Lead Response of 12-Lb. (Reid Vapor Pressure) Borger Natural Gasoline

Inasmuch as a mixture of *iso*pentane and pentane-free natural gasoline is superior to 12-pound natural gasoline for blending with *iso*octane, some representative data are presented on the catalytic desulfurization of so-called "pentane-free" natural gasolines. Table 2 gives the inspection data on the Borger gasoline before and after the bauxite treatment, whereas Figure 3 shows the TEL curves. The treated product with 1 ml. TEL rates 8.1 octane numbers higher than the untreated; with 3 ml. TEL, the improvement is 7.7 octane numbers. It should be noted that the desulfurized gasoline with 1 ml. TEL has a rating of 75.0 octane number; whereas the undesulfurized gasoline with 3 ml. TEL rates only 74.3. In the treatment, the sulfur content was lowered from 0.057 to 0.005 percent—a reduction of 91 percent. The distillation and vapor-pressure characteristics were unchanged.

It may appear surprising at first thought that a naphtha of only 60 octane number should be considered a suitable blending stock in the manufacture of high-octane gasolines. However, a closer study of the data presented will reveal the fact that these pentane-free natural gasolines have extremely good TEL susceptibilities; so that in the manufacture of ethylized gasolines they are equal, and in some cases superior, to other naphthas of considerably higher clear octane numbers.

The pentane-free natural gasoline from Hobbs, N. M., had a considerably higher sulfur content, and a higher clear octane number, than the corresponding stock from Borger. The higher octane number would seem to be

TABLE 1

Average Tetraethyl-Lead Requirements of Borger 12-Lb. Natural Gasoline

	Undesulfurized	Desulfurized		
Sulfur, percent	0.037	0.008	0.004	0.002
Average Octane No., ASTM				
Initial	67.2	69.5	69.6	69.7
Plus ½ ml. TEL	72.2	76.5	76.8	77.0
Plus 1 ml. TEL	75.6	80.0	81.0	81.4
Plus 2 ml. TEL	79.6	82.0	84.3	84.9
Plus 3 ml. TEL	82.1	85.3	86.8	87.5
Plus 4 ml. TEL	84.0	87.6	89.2	89.7
Plus 6 ml. TEL	86.6	91.2	92.8	93.2
TEL saving to 76 octane No., percent		58	60	62
TEL saving to 82 octane No., percent		46	57	62
TEL saving to 88 octane No., percent		43	52	56

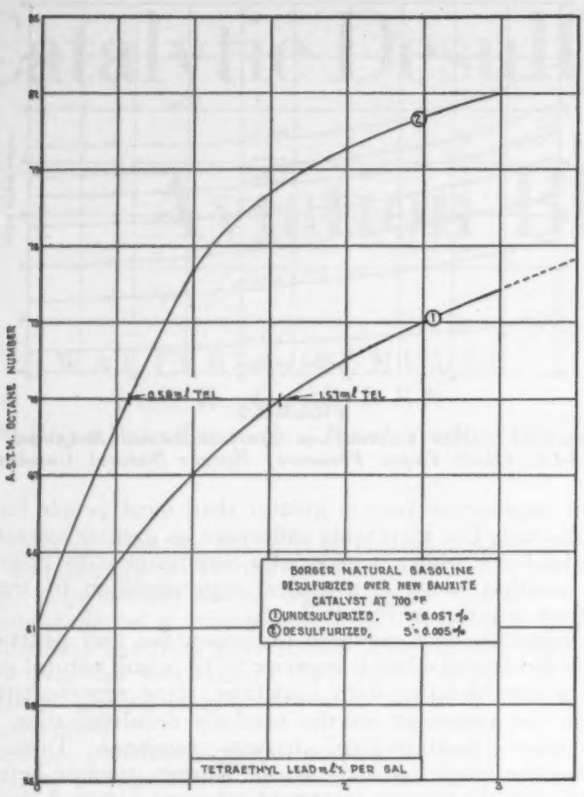

FIGURE 3

6-Lb. (Reid Vapor Pressure) Borger Natural Gasoline Before and After Desulfurization

an added advantage for aviation-gasoline blending, but this is offset by the poor lead response. The undesirable sulfur compounds may be removed, however, by the bauxite treatment mentioned above. Table 3 shows the inspection tests on this gasoline before and after treatment at a temperature of 750 °F. and at a flow rate equivalent to 325 barrels of gasoline per day per ton of bauxite catalyst. The sulfur content was reduced from 0.096 to 0.008 percent.

The data presented in Tables 4 and 5 are illustrative of the effect of catalytic desulfurization when applied to a light straight-run gasoline previously given extensive chemical treatment and fractionation. This gasoline, obtained from New Mexico crude, had only 0.013 percent sulfur left in it at the time the catalytic treatment was made. Obviously, catalytic desulfurization would not be applied at this point in the processing, but the results do show the increased benefits to be derived from complete desulfurization. As is usual for low-sulfur straight-run gasolines, there was no change in the initial octane number of the gasoline on the catalytic treatment. However, upon the addition of 1 ml. tetraethyl lead per gallon, the desulfurized gasoline showed a response of 10.9 octane numbers, whereas the undesulfurized had a response of only 9.0 units. Although the improvement is not large in terms of octane numbers, the percentage of *iso*octane in 100-octane fuel can be decreased through the use of the more-completely desulfurized straight-run naphtha.

TABLE 2

Desulfurization of Borger Pentane-free Natural Gasoline

	Before Desulfurizing	After Desulfurizing
ASTM Octane No.:		
0 ml. TEL per gallon	59.2	61.1
Plus 0.5 ml. TEL per gallon	63.5	68.9
Plus 1.0 ml. TEL per gallon	66.9	75.0
Plus 2.0 ml. TEL per gallon	71.6	79.8
Plus 3.0 ml. TEL per gallon	74.3	82.0
TEL to 76 octane No., ml. per gallon	3.90	1.12
Saving per gallon, ml.	....	2.78
Sulfur, per cent	0.057	0.005
Reid vapor pressure, lb. per sq. in	6.40	6.50
Gravity, deg. API	71.8	71.9
ASTM Distillation, in Deg. F.:		
Initial boiling point	121	120
5 percent point	137	138
10 percent point	142	143
20 percent point	147	148
30 percent point	152	153
40 percent point	157	158
50 percent point	164	164
60 percent point	172	173
70 percent point	182	183
80 percent point	198	200
90 percent point	226	228
95 percent point	263	265
End point	380	384
Recovery, percent	98.2	98.2
Residue, percent	1.0	1.0
Evaporated at 212° F., percent	85.5	85.0

BLENDS OF *ISO*OCTANE WITH UNDESULFURIZED AND DESULFURIZED NAPHTHAS

The increase in lead response of blends of *iso*octane with catalytically-desulfurized naphtha nearly always is directly proportional to the amount of such naphtha in the blends, the effect being undiminished on mixing with other products. Thus, the monetary savings to be derived through catalytic desulfurization of the blending naphtha may come about in two ways, viz.: 1, the increase in production of a given grade of aviation gasoline from a given volume of *iso*octane; and, 2, increased octane numbers obtainable with given blending formulas and TEL contents. As the increased production of given grades of high-octane gasoline constitutes a tangible and important basis for appraising the benefits to be derived from the catalytic desulfurization, data are presented hereinafter for three of the four gasolines previously discussed. The Borger 12-pound gasoline obviously has an octane-number-vapor-pressure relationship inferior to the other three gasolines.

For the *iso*octane-blending experiments described in

TABLE 3

Hobbs Pentane-free Natural Gasoline

	Before Desulfurizing	After Desulfurizing	Improvement
ASTM Octane No.:			
0 ml. TEL per gallon	65.6	65.6	0.0
Plus 1 ml. TEL per gallon	71.4	77.7	6.3
Plus 2 ml. TEL per gallon	76.0	82.3	6.3
L-3 Octane No.:			
0 ml. TEL per gallon	64.2	64.2	0.0
Plus 1 ml. TEL per gallon	71.6	78.4	6.8
Plus 2 ml. TEL per gallon	76.6	83.9	7.3
Reid vapor pressure, lb. per sq. in.	5.20	5.20	..
Gravity, deg. API	68.6	68.5	..
ASTM Distillation, in Deg. F.:			
Initial boiling point	145	141	..
5-percent point	155	153	..
10-percent point	161	157	..
20-percent point	164	161	..
30-percent point	166	166	..
40-percent point	169	169	..
50-percent point	174	173	..
60-percent point	179	178	..
70-percent point	189	188	..
80-percent point	203	203	..
90-percent point	229	227	..
95-percent point	256	252	..
End Point	314	311	..
Recovery, percent	98.7	98.8	..
Residue, percent	0.8	0.8	..
Loss, percent	0.5	0.4	..
Evaporated at 212° F., percent	85.0	84.5	..

the following paragraphs, the commercial *iso*octane used was one with 91 octane number and a very superior lead response. All blends were *iso*pentanized (about 20 percent usually) to 7.0-pound vapor pressure.

TABLE 4
New Mexico Light Straight-run Gasoline

	Before Catalytic Desulfurization	After Catalytic Desulfurization
ASTM Octane No.:		
0 ml. TEL per gallon	76.0	76.0
Plus 1 ml. TEL per gallon	85.0	86.9
Plus 2 ml. TEL per gallon	88.7	90.0
Plus 3 ml. TEL per gallon	91.2	92.2
Reid vapor pressure, lb. per sq. in.	11.2	11.25
Gravity, deg. API	76.1	76.2
Color, Saybolt	+30+	+30+
ASTM Distillation, in Deg. F.:		
Initial boiling point	98	95
5-percent point	112	113
10-percent point	121	119
20-percent point	129	128
30-percent point	137	136
40-percent point	143	143
50-percent point	150	150
60-percent point	157	156
70-percent point	163	163
80-percent point	170	169
90-percent point	180	180
95-percent point	190	191
End point	204	206
Recovery, percent	98.1	98.8
Residue, percent	0.3	0.4
Loss, percent	1.6	0.8

BORGER "PENTANE-FREE" NATURAL GASOLINE

To determine the effect of partial desulfurization, this material was desulfurized to varying degrees with the following results, expressed in terms of the increase in production of 100-octane gasoline with 3.0 ml. TEL. With further desulfurization, for example to the 0.005 shown in Table 2, the increased production of 100-octane gasoline, of course, would be much greater than the above figures.

Sulfur Content "Pentane-free" Natural Gasoline	Percent *Iso*octane Required	Percent Increased Production of 100-Octane Gasoline
0.056 (undesulfurized)	66.0	....
0.017	58.5	12.8
0.013	55.2	19.6

HOBBS "PENTANE-FREE" NATURAL GASOLINE

Because of the favorable anti-knock characteristics of this aviation natural gasoline, extensive blending experiments were conducted with *iso*octane. A comparison of the blending values of the pentane-free natural gasoline before and after desulfurization is shown in Figure 4, wherein the percent of *iso*octane base is plotted against the octane number. As previously mentioned, all of the blends contained sufficient *iso*pentane to give 7.0-pound Reid vapor pressure.

TABLE 5
New Mexico Light Straight-run Gasoline

	Before Catalytic Desulfurization	After Catalytic Desulfurization
Color, Saybolt	+30+	+30+
Doctor test	Negative	Negative
Sulfur, percent	0.013	0.0016
Copper-strip test at 122 deg. F., hours	5+	5+
Copper-dish gum, mg. per 100 ml.	1	2
ASTM gum, mg. per 100 ml.	0	0
Oxygen-bomb stability, min.	300+	300+
Acid heat, deg. F.	4	4

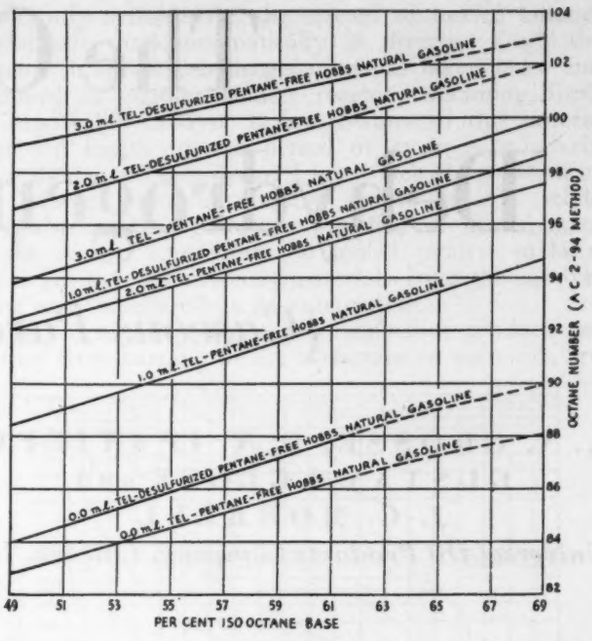

FIGURE 4
Comparison of the Blending Value of Undesulfurized and Desulfurized Pentane-free Hobbs Natural Gasoline in the Manufacture of Aviation Gasoline

From the data on which Figure 4 was derived, the calculations shown in the following tabulation have been made.

Kind of Finished Gasoline		Percent *Iso*octane in Finished Gasoline Containing:		Percent Increase in Production by Desulfurization
Octane No.	Ml. TEL.	Undesulfurized Pentane-free Natural Gasoline	Desulfurized Pentane-free Natural Gasoline	
92	0.5	70.0	58.5	19.7
100	3.0	69.2	54.2	27.7
87	1.0	44.6	29.3	52.2

In addition to the decrease of *iso*octane, there were also smaller decreases in the *iso*pentane used in the blends with desulfurized gasolines. If the refiner does not use *iso*pentane in the aviation blends, the increase in finished-gasoline production is even greater than shown above.

With given blending formulas and TEL contents within the range indicated, the following increases in octane number are obtainable through desulfurization of the pentane-free natural gasoline used in the blends:

Ml. TEL	Increase in Octane No.
0.5	3.0
1.0	4.0
1.5	4.3
2.0	4.7
3.0	5.3

Thus, the octane number of the finished gasoline was increased as much as five units merely through desulfurization of the naphtha. Such a sizeable improvement in this high-octane bracket obviously warrants considerable attention.

NEW MEXICO STRAIGHT-RUN GASOLINE

In 7.0-pound *iso*octane blends of the New Mexico straight-run gasoline before and after desulfurization,

(Continued on page 137)

The Catalytic Dehydrogenation Process

(*Gaseous Paraffins to Olefins*)

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ANOTHER commercial catalytic process has been developed which adds enormously to our potential gasoline supply for aviation and motor-vehicle use. This process is called catalytic dehydrogenation, and applies to the conversion of gaseous paraffins, except methane, into the corresponding olefins and hydrogen. The paraffins are derived from natural gas, casinghead gas, refinery gases, and gases from other sources such as coal. In view of the present intense interest in *iso*octane as an aviation fuel, the production of *iso*- and *n*butenes is of primary importance.

Thermal cracking of paraffin gases is a competing source of olefins. However, catalytic dehydrogenation gives a much greater yield, both once-through and ultimate, as well as a much faster production rate of olefins than thermal cracking. In the thermal reaction, substantial carbon-to-carbon bond splitting takes place; e. g., in the case of *n*butane the yield of *n*butenes does not exceed, under best conditions, 15 percent of the charge.

Catalytic dehydrogenation of *n*- and *iso*butane and of propane to the corresponding olefins is a highly-selective reaction and produces, on a commercial scale, 85 to 95 percent of the theoretical yield of olefins from paraffins. Actually, in the laboratory on a recycle basis, more than 95 percent of the theoretical yield of olefins from paraffins has been obtained. The catalytic reaction suppresses the occurrence of side reactions, such as the formation of methane and ethane from propane and butanes. Also, when processing butanes, it suppresses propene formation, and produces principally butenes.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

A DIAGRAMMATIC comparison of catalytic vs. thermal results with *n*butane is shown in Figure 1. The upper part of the figure shows the percentage of butenes in the exit gas, whereas the lower part shows the corresponding production rates for a given conversion at the temperature and pressure conditions indicated.

Some of the previous work having an important bearing on the present subject is referred to hereinafter.

Frey and Huppke,[1] of the Phillips Petroleum Company, found that the gaseous paraffins were dehydrogenated at atmospheric pressure in the presence of a chromic-oxide gel at temperatures of from 350 to 500° C. For example, in the case of *n*butane at 500° C., a yield of 14 percent unsaturates was obtained which were composed of 25 percent 1-butene, 75 percent 2-butene, and 1 percent butadiene. The oxide-gel catalyst loses its activity in the course of a few hours.

Grosse and Ipatieff[2] presented a paper at the Milwaukee meeting of the American Chemical Society, September 6, 1938, in which they described the fundamentals of the catalytic-dehydrogenation reaction for the conversion of paraffinic hydrocarbons to the corresponding olefins. It is based on the use of catalysts, consisting of oxides of the transition metals of the fourth, fifth and sixth groups of the periodic system on especially-developed supports, such as alumina. Catalysts consisting of chromium oxide on alumina were found to be of particular importance. These catalysts have a long life, and are highly selective. They lead the conversion in accordance with the general dehydrogenation equation:

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$$

The scission of the carbon-to-carbon bond—leading to the formation of carbon, methane, and other degradation products—practically has been suppressed completely. Overall conversions of *n*butane into *n*butenes, *i*butane into *i*butene, propane into propene, and ethane into ethylene of 90 to 95 percent of the theoretical are obtained. The process is also a source of practically pure hydrogen (more than 90 percent). The latter is produced in amounts equal to the volume of olefin in accordance with the foregoing equation. The description of the chemistry and thermodynamics of the reaction, the identification of the reaction products, and the preparation of a laboratory catalyst are described in the Grosse and Ipatieff paper. The process operates usually at pressures of around one atmosphere in the range of 500 to 750° C., (and at space velocities from 500 up to 10,000 or higher), depending upon the charging stock.

Burgin, Groll, and Roberts,[3] of the Shell Development Company, described practically simultaneously a dehydrogenation process using activated alumina as a catalyst promoted by various metal compounds, particularly chromium oxide. A slight amount of water—referred to as a mono-molecular layer—on the catalyst is stated to be necessary for the reaction. They state that the reaction does not occur in the absence of water. In general, their results are comparable to those presented by Grosse and Ipatieff.

Typical results with *n*butane in connection with the present work, illustrating the influence of temperature and space velocity on conversion, are shown in Figure 2. A chromium-oxide on alumina catalyst was used.

CATALYTIC-DEHYDROGENATION PROCESS

The process best may be described by reference to the flow chart of Figure 3. The charging stock, which may consist of butanes or propane or a mixture thereof, for purposes of illustration here will consist essentially of a mixture of *iso-* and normal butanes.† The butanes are passed through a heating coil in a furnace, where they are heated to a temperature at which their substantial conversion into butenes will occur in the presence of the catalyst.

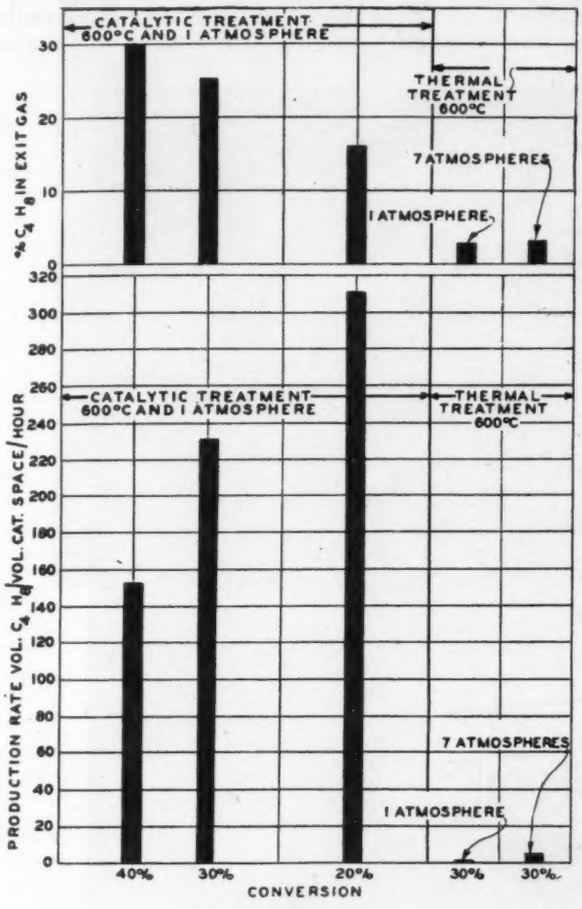

FIGURE 1
Comparison of Catalytic and Thermal Treatment of nButane.

The heated butanes are passed from the heating coil to one of a plurality of reactors, each of which alternately is employed for conducting the dehydrogenating reaction and for reactivating the catalyst. The reactors are of heat-exchanger type, having a plurality of tubular elements in which the catalyst is disposed and through which the reactants and resulting reaction products are passed. A jacket is provided about the tubular elements, and a convective fluid may be circulated through the jackets of the reactors at a temperature regulated to control the temperature of the reaction taking place within the tubes. The material of the reactors must be such so as not to poison the catalyst by deposition of iron oxides. The catalyst is of the chromium-oxide on alumina type. It is not poisoned by sulfur compounds nor carbon monoxide.

During dehydrogenation in each reactor, carbonaceous materials are deposited on the catalyst, and progressively reduce its activity. To keep the catalyst in a sufficiently active state, the stream of heated butanes periodically and automatically is diverted from the reactor in which dehydrogenation has taken place and supplied to another similar reactor containing fresh or reactivated catalyst. It is a feature of this process that the length of the period or cycle is relatively very short—of the order of 1 hour. Dehydrogenation of the butanes continues in the second reactor, while oxygen-containing gases are supplied in heated state to the reactor containing the fouled catalyst to burn the deposited carbonaceous materials from the catalyst mass and thereby effect its reactivation.

Spent reactivating gases and combustion products resulting from burning of the carbonaceous materials are discharged from the reactor in which reactivation of the catalyst is taking place, and are recycled for further use after their temperature and oxygen content have been readjusted to the desired value.

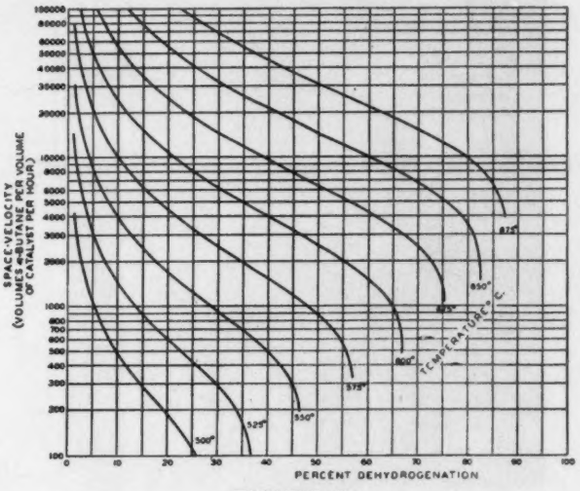

FIGURE 2
Catalytic-Dehydrogenation of nButane

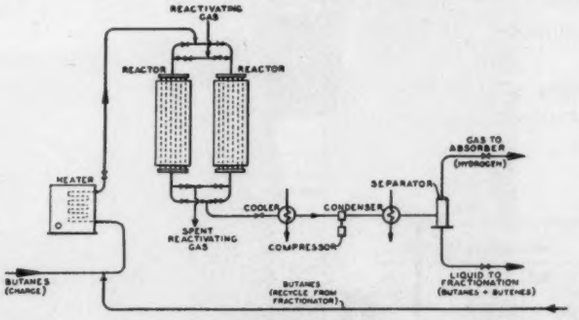

FIGURE 3
Catalytic Dehydrogenation Process

The products of catalytic dehydrogenation consist principally of *iso-* and normal butenes, unconverted butanes, hydrogen, and a small amount of lighter hydrocarbon gases such as methane, ethane and ethene, propane and propene. These products continuously are withdrawn from the reactor, in which the dehydrogenating reaction is taking place, through a suitable cooler to a compressor. After compression, the gases are cooled further, and are passed to a separator from which a liquefied fraction, consisting essentially of butenes and unconverted butanes, and a gaseous fraction consisting essentially of hydrogen and the lighter hydrocarbon gases, separately are withdrawn. The gases from the separator are passed to an absorber in which their relatively-heavy components, including any uncondensed

† If desired, the *n*butane, either partly or wholly, may be converted into *i*butane by means of the catalytic-isomerization reaction.

butanes and butenes, are separated by absorption from a lighter gaseous fraction rich in hydrogen and suitable for use, when desired, to hydrogenate liquid products such as *iso*octene resulting from polymerization of the butenes. The liquid fractions from the separator are supplied to suitable fractionating or stabilizing equipment, in which they substantially are freed of undesirable dissolved light gases; and the resulting stabilized product may be sent to storage or directly to a catalytic-polymerizing process for conversion of the butenes into liquid polymers of high anti-knock value boiling within the range of gasoline. Unconverted butanes may be recycled back to the process.

Illustrations of the pilot or semi-commercial plant at Riverside, with a daily processing capacity of about 100,000 cubic feet of gas, are shown in Figures 4 to 8.

RESULTS

Typical results obtained in the semi-commercial plant operation are given in Table 1. Three representative commercial charging stocks consisting of: *a*, mainly *n*butane; *b*, mainly *iso*butane; and *c*, a 1:1 *n*- and *i*butane mixture were used.

The periods on stream refer to the beginning of the catalyst's life. The analyses of the inlet and outlet gases are averages over the consecutive processing

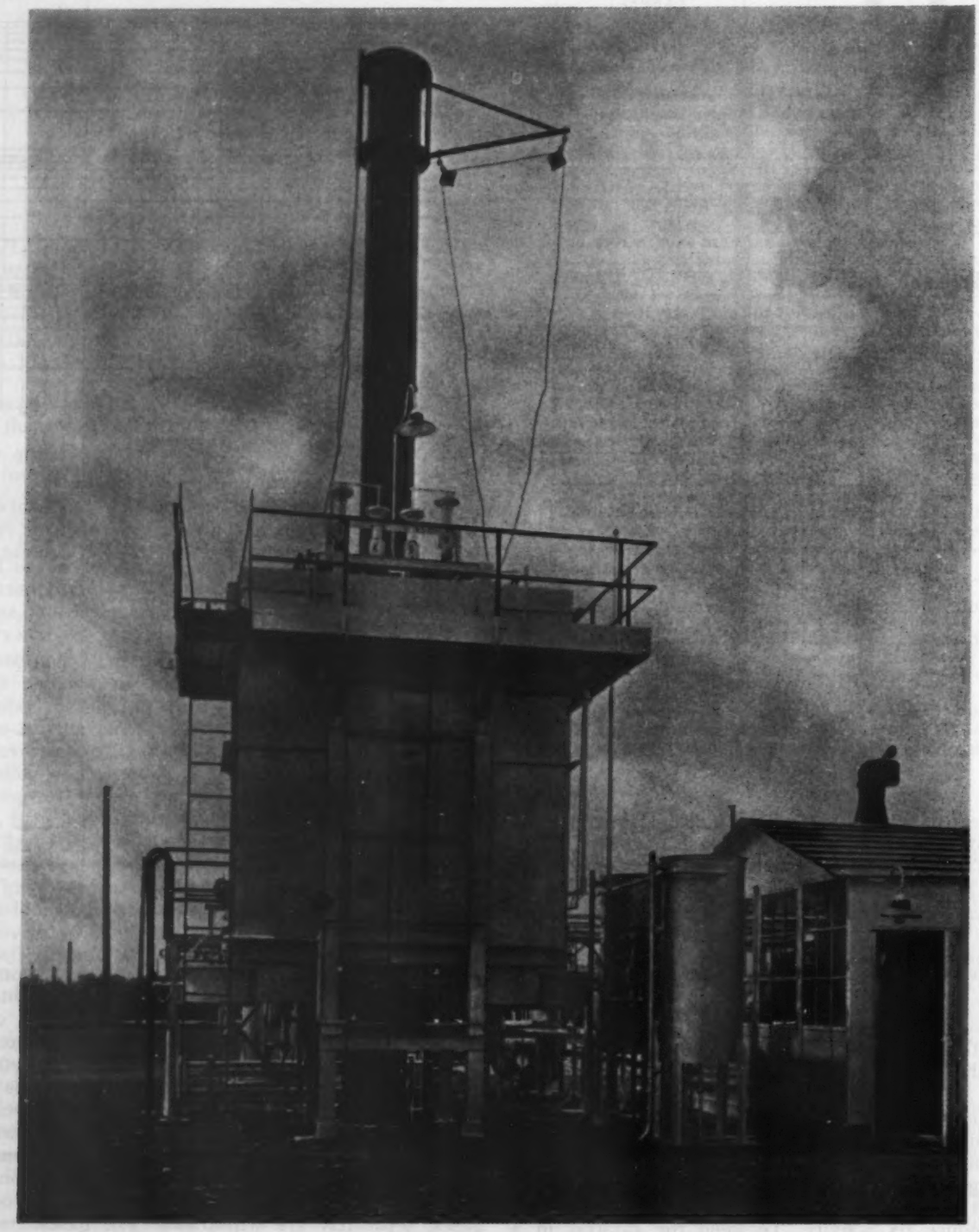

FIGURE 4
Semi-commercial Plant—Dehydrogenation Process. Front View.

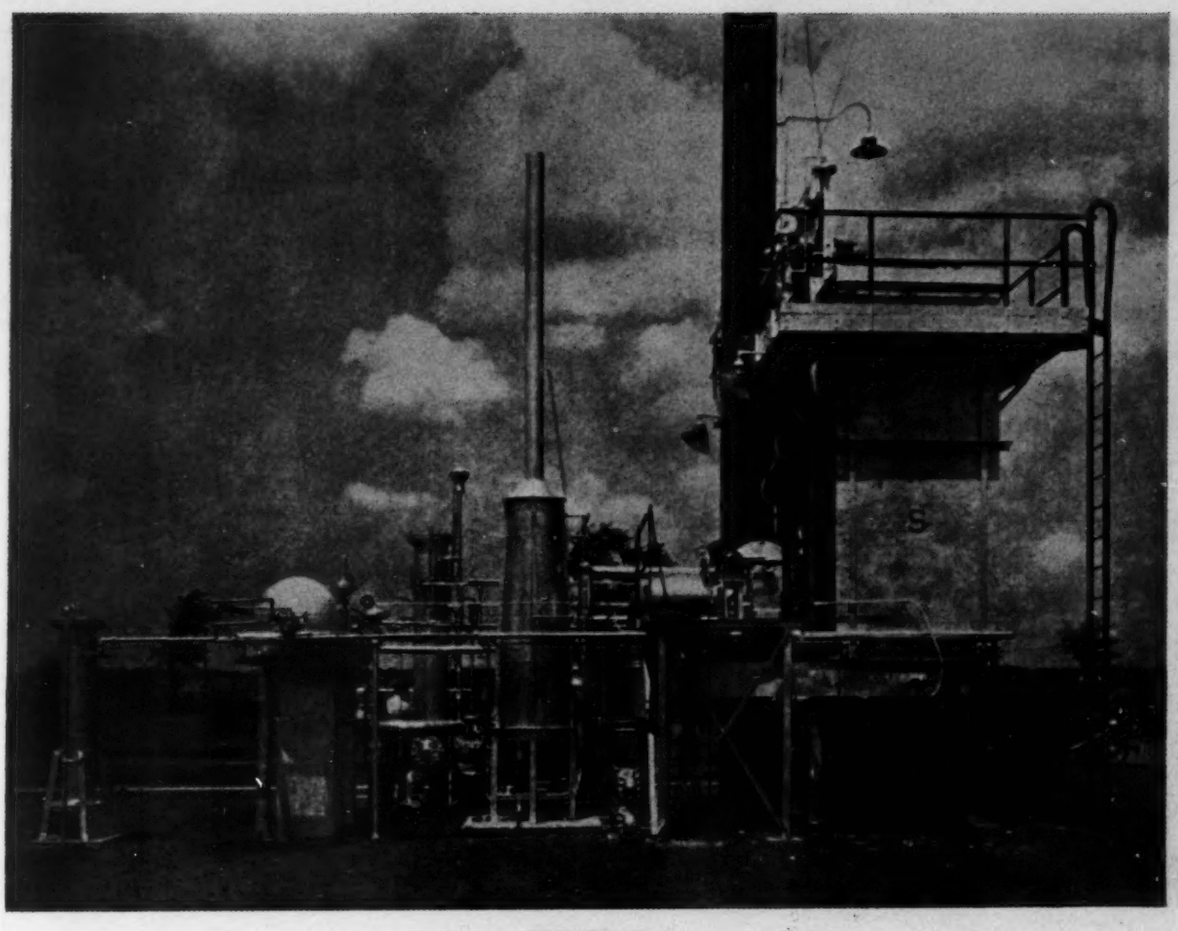

FIGURE 5
Semi-commercial Plant—Dehydrogenation Process. Side View.

periods indicated in the first row. Our definitions of conversion and efficiency are given in the table. The yield per pass is defined as the product of conversion times efficiency.

Particular attention is drawn to the efficiency figures which all lie between 85 and 95 percent of the theoretical.

It may be seen also that the volume of hydrogen agrees with the dehydrogenation equation; for it equals, in the first approximation, the sum of the volumes of the butylenes.

The performance of our catalysts over long periods of time is illustrated in Figure 9. The practically-

TABLE 1

	Mainly *n*Butane			1:1 *n*- and *i*Butane Mixture			Mainly *Iso*butane		
Periods on stream, from start	290–1	345–8	366–9	148–50	184–7	214–7	62–65	88–91	109–112
Space velocity, per hour	1,460	1,465	1,450	1,440	1,455	1,395	1,320	1,360	1,385
Average temperature of catalyst, °F	982	976	987	999	996	996	1,000	1,020	1,021
Inlet pressure, lb., per sq. in	52	52	52	52	51	52	60	62	69
Outlet pressure, lb., per sq. in	20	18	18	20	20	20	5	5	5
Inlet Gas:									
Composition: Mole percent									
C_3H_8	0.8	....	1.0	2.7	3	3.5	4.6	8.8	9.4
i-C_4H_{10}	13.1	16.8	16.7	58.8	40	42.0	77.1	78.7	79.0
n-C_4H_{10}	86.1	82.3	82.3	37.2	56	54.2	18.3	12.5	11.6
C_5H_{12}*	....	0.9	....	1–3	1	0.3	....	....	....
Outlet Gas:									
Composition: Mole percent									
H_2	17.3	18.0	18.1	21.2	18.8	20.2	18.4	21.6	20.1
CH_4	1.4	1.6	1.7	1.9	1.8	3.2	1.8	2.0	1.2
C_2H_4 and C_2H_6	0.5	0.5	0.19	0.2	0.1	0.5	....	....	0.7
C_3H_6	0.4	0.3	0.9	1.0	1.0	0.8	1.2	1.8	1.6
C_3H_8	1.5	1.3	1.5	4.4	5.2	3.4	4.4	7.4	8.1
i-C_4H_8	3.3	2.9	3.2	10.9	7.0	6.9	13.3	12.7	11.6
n-C_4H_8	15.9	15.7	17.0	9.9	12.2	12.1	3.4	5.9	5.5
C_4H_{10}	59.7	59.7	56.7	50.4	53.3	52.7	57.5	48.6	51.2
Conversion:									
Moles C_4H_8 converted per 100 moles C_4H_{10} charged	25.7	24.9	28.1	31.6	29.5	29.0	24.9	30.8	28.1
Conversion corrected to 1,050 °F. and 2,000 space velocity per hour	36	36	37	38	37	36	31*	33*	30*
Efficiency (mole C_4H_8 per 100 mole C_4H_{10} converted)	93	94	91	89	86	88	88	86	86
Yield per pass (mole C_4H_8 per 100 C_4H_{10} charged)	24	23	26	28.2	25.4	25.6	21.8	26.5	24.0
Yield per pass corrected to 1,050 °F. and 2,000 space velocity per hour	33	34	34	34	32	32	27	28	26

* Lower conversions partly due to high propane content of charge.

FIGURE 6
Semi-commercial Plant—Dehydrogenation Process. Bottom of Furnace.

constant activity and selectivity over a period of approximately 2000 hours proves the ruggedness and stability of the catalyst.

*ISO*OCTANE PRODUCTION PROCESS VIA DEHYDROGENATION—POLYMERIZATION—HYDROGENATION

The dehydrogenation process may be described also in connection with the flow diagram (Figure 10) of the process for the production of *iso*octane. This process is applicable to the production of aviation fuel from mixtures of *iso*- and normal butanes.

The charging stock consists essentially of butanes. The proportion of *iso*butanes to *n*butanes varies from 15 to more than 75 percent. The octane rating of the hydrogenated polymer increases with the increase of *iso*butane in the charge.

The butanes are supplied at relatively low pressure to the preheater of the dehydrogenation unit, from which it emerges at approximately 1075° F., and is directed to the dehydrogenation catalyst zone. The catalyst is of the chromium-oxide on alumina type; and is contained in vertical tubes, externally heated by hot combustion gases. The butane passes through the catalyst at a high space velocity, and approximately 25 percent of the charge is dehydrogenated. The gases leave the catalyst tubes at a pressure only slightly above atmospheric, and at a temperature of approximately 1125° F.

The butane-butene mixture and hydrogen from the dehydrogenation system are cooled and compressed to approximately 100 to 200 pounds per square inch, and then are passed to an adsorber where the hydrogen is separated. A stripper is provided for removing the butane-butene mixture from the absorption oil, which is cooled and returned to the absorber.

The butane-butene product is pumped at high pressure to the polymerization unit of the process employing the solid UOP phosphoric-acid catalyst. The temperature employed here is 250 to 350° F., and the pressure 750 to 1500 pounds. The temperature is controlled by a water-jacketing system around the reactor tubes. At higher temperatures, a greater proportion of the normal butenes is polymerized, but yields a lower octane number of the hydrogenated product. The temperature, therefore, is determined by the octane number of the product desired. Steam produced from the reactor jackets, due to the exothermicity of the reaction, is used to preheat the feed.

The polymer is debutanized, rerun, and catalytically hydrogenated to end-point aviation gasoline of approximately 97 octane number.

Only about 10 percent bottoms (heavy polymers such as trimers) are produced in rerunning. The unreacted normal butenes from the debutanizer are led to a secondary polymerization stage, generally operated at higher temperature (i.e., 475° F.) than in the selective-polymerization section. Temperature control is similar to that in the selective-polymerization operation. The polymer product of the butane-selective-polymerizing step passes through the stabilizer, where the liquid polymers are separated from butanes. The butanes are

returned to the dehydrogenating step of the process. The polymer, when rerun and hydrogenated, yields a product of approximately 85 octane number.

The hydrogenation unit is operated alternately on the selective polymer and the residual butene polymer. A nickel-oxide catalyst is employed for hydrogenation. The hydrogen produced by dehydrogenation of the butanes is twice that required for hydrogenation of the polymer products. The rerun polymer and the hydrogen gas are supplied at a pressure of 150 to 200 pounds per square inch to the hydrogenation reactor tubes. As the nickel catalyst is sensitive to sulfur compounds, it is preferable to desulfurize the butane before dehydrogenation. If not desulfurized, the material first is passed through a guard reactor—which is filled with spent hydrogenation catalyst for removing sulfur-compound impurities—and then is passed through two reactors, in series—being hydrogenated by the gas in concurrent flow. As hydrogenation is also an exothermic reaction, essentially the same method of temperature control as in polymerization is used. The temperature is maintained at approximately 350° F., and the outlet pressure at about 35 pounds per square inch, or just sufficient to depress the vaporization of excessive

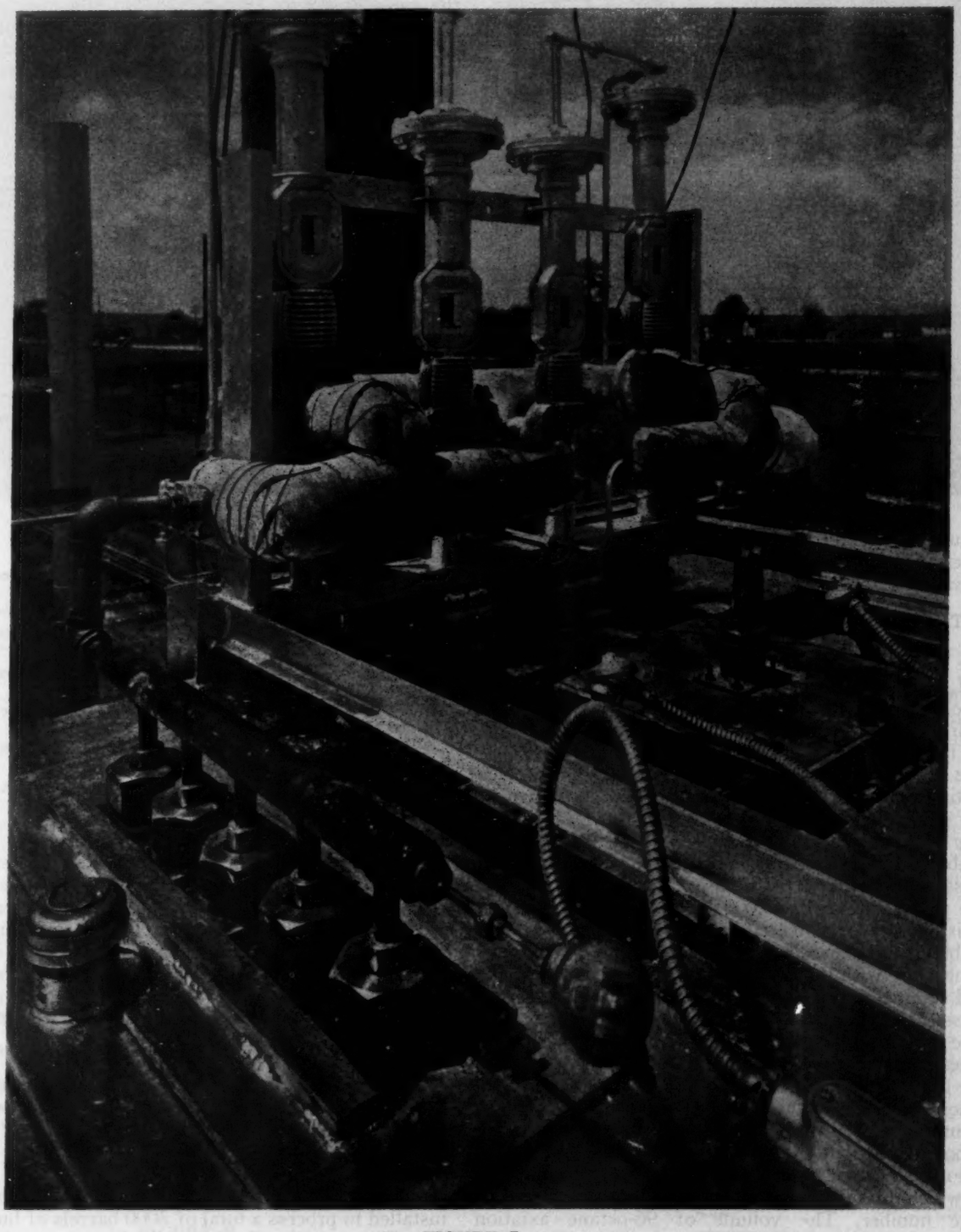

FIGURE 7
Semi-commercial Plant—Dehydrogenation Process. Top of Furnace.

TABLE 2
Hydrocarbon Gases Produced in the United States in 1939
(Billions of Cubic Feet)

	Natural Gas	Refinery Gas—Crude Distillation	Cracked Gas	Total
Cubic Feet	2,500	250	350	3,100
	Percent	Percent	Percent	
Methane	69	61	53	....
Ethane	14	21	15	....
Propane	9	12	5	....
Butanes	5	4	2	....
Ethene	..	..	6	....
Propene	..	..	13	....
Butenes	..	..	6	....

TABLE 3
Hydrocarbon Gases in 1939
(Billions of Cubic Feet)

	Natural Gas	Refinery Gas—Crude Distillation	Cracked Gas	Total Hydrocarbon Gas (Cubic Feet)
Methane	1,725	152.5	185.5	2,063.0
Ethane	350	52.5	52.5	455.0
Propane	225	30.0	17.5	272.5
Butanes	125	10.0	7.0	142.0
Ethene	....	....	21.0	21.0
Propene	....	....	45.5	45.5
Butenes	....	....	21.0	21.0

TABLE 4
Ethene, Propene, and Butenes Potentially Available by Catalytic Dehydrogenation and Cracked Gases
(Billions of Cubic Feet Annually)

Ethene	420.5
Propene	290.5
Butenes	148.8

amounts of *iso*octane in the spent gas. The hydrogenated product from the selective-polymerization step consists essentially of *iso*octanes.

STATISTICAL DATA ON POTENTIAL PRODUCTION OF BUTENES AND *ISO*OCTANE

The following statistical data, supplied by Gustav Egloff, are quoted to illustrate the economic possibilities of the process. The approximate volumes of hydrocarbon gases available in the United States in 1939 are given in Tables 2 and 3.

The yearly volumes of ethene, propene, and butenes potentially available in the United States are shown in Table 4.

The potential polymer gasoline of 81 octane number available from the ethene, propene, and butenes—on the assumption that it is all used for this purpose—is at the yearly rate of 8,345,000,000 gallons. The breakup of this volume of potential polymer gasoline is shown in Table 5, and is based on only 25 percent of the ethene polymerizing with the propene and butenes, which is the actual commercial performance when using the catalytic process of polymerization.

The polymer gasoline of 82 octane number from butenes may be used as motor fuel, or blended with lower-grade gasoline to enhance its octane rating. When aviation gasoline is the desired product, the butenes present in cracked or dehydrogenated gases selectively are polymerized so as to produce *iso*octenes by the reaction of normal butene and *iso*butene in the ratio of 1:1, which in turn is converted into *iso*octanes of 96 octane number. The volume of 96-octane aviation gasoline potentially available from the butenes is more than 2,180,000,000 gallons a year. The normal butene left over in the residue gas from the first polymerization reaction is subjected to polymerization in a second step which, upon hydrogenation, produces a saturated 85-octane aviation-gasoline stock. The annual volume potentially available of this product is 1,095,000,000 gallons.

The potential aviation and polymer gasolines from the volumes of starting gases given in Table 4 are shown in Table 6.

A number of economic situations exist when it is more desirable to alkylate *iso*butane with ethene, propene, or butenes than to use the combination processes of polymerizing and hydrogenation. It is estimated, as an average, that normal and *iso*butane are present in the ratio of 25 to 75 percent. This means that there is potentially available about 35,500,000,000 cubic feet *of iso*butane in the gases listed in Table 3.

The thermal alkylation of combining *iso*butane with ethene at high temperature and pressure, producing

TABLE 5

FROM:	81-Octane Polymer Gasoline (Gallons)
Ethene	420,000,000
Propene	4,650,000,000
Butenes	3,275,000,000
Total	8,345,000,000

TABLE 6
Aviation and Motor Gasoline
(Gallons)

	80-Octane Polymer Gasoline	85-Octane Aviation Base	96-Octane Aviation Base
Ethene	420,000,000	.....	.....
Propene	4,650,000,000	.....	.....
Butenes	.....	1,095,000,000	2,180,000,000

TABLE 7
Aviation Gasoline Potentially Available from Hydrocarbon Gases

Process	Gallons	Octane No.
Dehydrogenation, Polymerization, Hydrogenation (from butanes-butenes-hydrogen)	2,180,000,000 1,095,000,000 3,275,000,000	96 85 92 average
Thermal Alkylation:		
Neohexane	1,290,000,000	95
*Iso*butane and ethylene		
Sulfuric-acid alkylation (*iso*butane and butenes)	1,715,000,000	93

neohexane of 95 octane rating, has a yearly potential production of 1,290,000,000 gallons, on the assumption that all the *iso*butane available is used in this process.

The catalytic sulfuric-acid alkylation process[4] may use propene and butenes with *iso*butane to form alkylate. The volume of alkylate from propene and *iso*butane potentially available, if all the *iso*butane were used, would be 1,500,000,000 gallons of 85 octane rating. If butenes are used for alkylation with *iso*butane, the yearly volume available of alkymer would be 1,715,000,000 gallons of 93 octane rating.

A comparison of the yearly potential aviation gasoline available, if each one of the three processes were used alone, is given in Table 7.

COMMERCIAL PLANTS

Three commercial dehydrogenation plants are being installed to process a total of 3000 barrels of butanes per day. The resulting butenes will be converted into *iso*octanes and hydrogenated to *iso*octanes of 97 octane rating at the daily rate of about 2200 barrels.

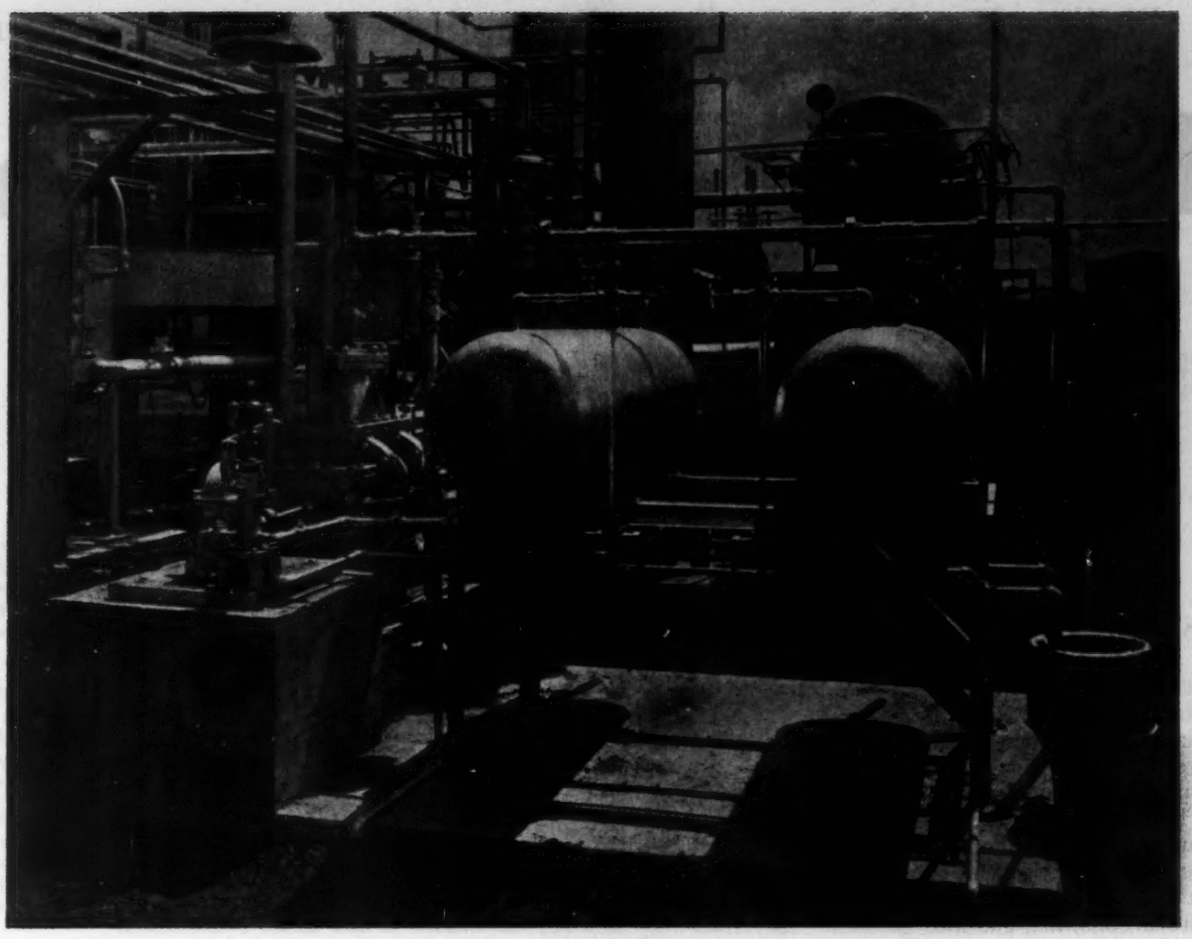

FIGURE 8
Semi-commercial Plant—Dehydrogenation Process. Refrigeration System.

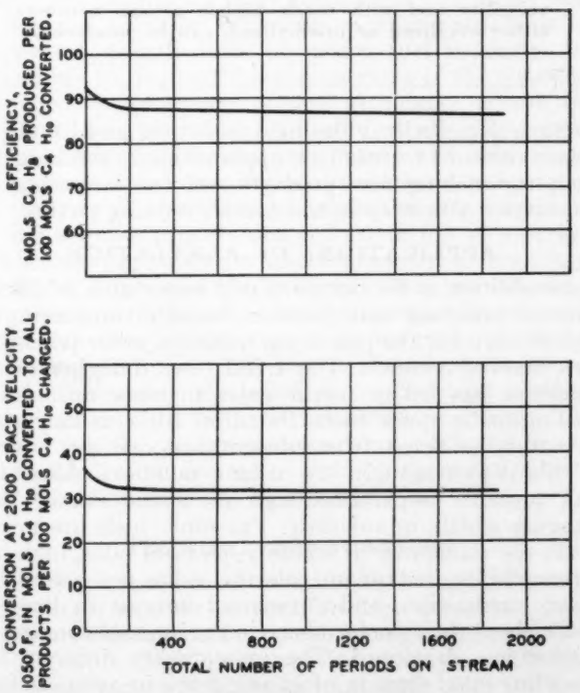

FIGURE 9
Pilot Plant Performance of Catalyst with nButane During a 75-Day Run.

ACKNOWLEDGMENT

The authors wish to take this opportunity to acknowledge the valuable contributions and assistance of the entire staff of the Universal Oil Products Company—particularly of the research, development, engineering research, and engineering departments, and of the pilot-plant group.

BIBLIOGRAPHY

[1] F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.* **25**, 54 (1933).
[2] A. V. Grosse and V. N. Ipatieff; see abstracts of the Milwaukee meeting *Am. Chem. Soc.*, Sept. 1938 (p. M-6); also *Ind. Eng. Chem.*, 1939 (in print).
[3] J. Burgin, H. Groll, and R. M. Roberts, *Natl. Petroleum News* **30** [36] R-432 (1938).
[4] S. F. Birch, A. E. Dunstan, and coworkers, *Oil Gas J.* **37** [6] (1938); Visser, British Patent 479,827; J. C. Morrell, U. S. Patent 2,169,809.

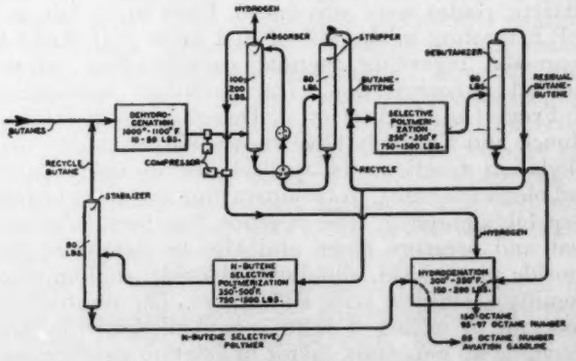

FIGURE 10
Isooctane Process via Dehydrogenation—Polymerization—Hydrogenation.

Phillips Petroleum Company Research Department Report On

Thermal Alkylation and Neohexane*

G. G. OBERFELL and F. E. FREY
Phillips Petroleum Company

ALKYLATION is a recently developed addition to conversion processes applicable to hydrocarbons. The alkylation reaction can be conducted either thermally or catalytically to produce isoparaffinic fuels of high octane number, the well known isooctane and other isoparaffins as well.

With non-selected conversion stock, such as ethane, propane, and butane, motor fuel can be produced in high yield by thermal alkylation in a two-stage process in which the lighter part of the stock can be cracked to produce olefins in one stage, which are reacted with the heavier part of the stock in a second, or alkylation, stage.

By selecting ethylene and isobutane as reactants, thermal alkylation at high pressures will produce neohexane, an isoparaffin of high octane number suitable for aviation fuel, but higher in volatility than isooctane. A commercial plant for producing neohexane is now under construction.

Neohexane has a high lead susceptibility, with 3.0 cc. TEL per gallon it is comparable to c.p. isooctane in anti-knock rating with 3 cc. TEL per gallon. When the aviation gasoline ordinarily used now in blending to high octane number fuels is replaced by suitable mixtures of neohexane and isooctane finished aviation gasolines of balanced volatility and with much higher octane numbers, either ethylized or unethylized, can be produced.

THE union of paraffins with olefins, usually designate alkylation, is a newcomer in the field of conversion processes. Alkylation is already of commercial importance and is taking its place alongside the other processes developed in recent years which give the petroleum industry a new versatility in the manufacture of finished products of various types and higher quality.

The term alkylation, like polymerization, has come to be used in the petroleum industry in a sense somewhat different from the strict chemical meaning. Polymerization processes convert light hydrocarbons into heavier hydrocarbons, i.e., gas into gasoline. Alkylation may be considered a special case of polymerization. Alkylation processes convert light hydrocarbons including at least some of a saturated type, directly into heavier hydrocarbons of a saturated type.

The alkylation of a paraffin by an olefin in its simplest form can be represented by the equation:

C_2H_4	+	C_3H_8	→	C_5H_{12}
olefin		paraffin		paraffin
ethylene		propane		pentane (n + iso)

wherein the paraffin propane combines with the olefin ethylene, both gases, to produce n-pentane and isopentane, two of the many paraffins in the motor fuel range.

The tradition of the chemical inertness of the paraffins may have had something to do with the belated discovery of the reaction, long known for the aromatic hydrocarbons. It was not until 1935 that experimental demonstrations of the paraffin-olefin union by thermal and catalytic routes were announced. Even so, as late as the A.P.I. meeting in the fall of that same year doubt was expressed regarding thermal paraffin-olefin union in thermal polymerization. The published investigations of Frey et al, Ipatieff et al, Dunstan, Birch et al, and Blunck and Carmody have shown the versatility of the alkylation reaction, its applicability to many paraffin and olefin reactants, to cycloparaffins as well as paraffins (see bibliography). The reaction has been effected by heat and pressure alone and also by catalysts; boron fluoride plus nickel, aluminum chloride, sodium chloroaluminate, sulfuric acid, and others. The production of isooctane by means of sulfuric acid alkylation is rapidly becoming an important factor in aviation gasoline manufacture. Research in the field is active, and alkylation seems destined to find new applications in the industry, both for making new products and for increasing the conversion efficiency in the overall refining picture.

APPLICATIONS OF ALKYLATION

In addition to the demonstrated importance of alkylation in isooctane manufacture, broadly considering its significance for the petroleum industry, other potentialities deserve mention. The trend toward higher octane numbers has led in recent years to more unsaturated and aromatic motor fuels. Paraffinic fuels, as they occur in nature or result from conventional refining, have as a rule discouragingly low octane numbers. Alkylation can produce isoparaffins high in octane number and ranging widely in volatility. Paraffinic fuels are unique from the standpoint of stability, pleasant odor, high lead susceptibility, maximum calorific value per pound and clean combustion, and a renewed interest in knowing more about their performance in the internal combustion engine has developed. The individuality different isoparaffins may show is of consequence in aviation fuels and in their application as chemical raw materials. Data to be presented will show differences between isooctane and neohexane in engine performance. The potential

* "The prefix *neo-* indicates the presence of a C attached by all four valences to other C atoms." (F. C. Whitmore, *Organic Chemistry*, Van Nostrand Co., New York, 1937, page 21.)

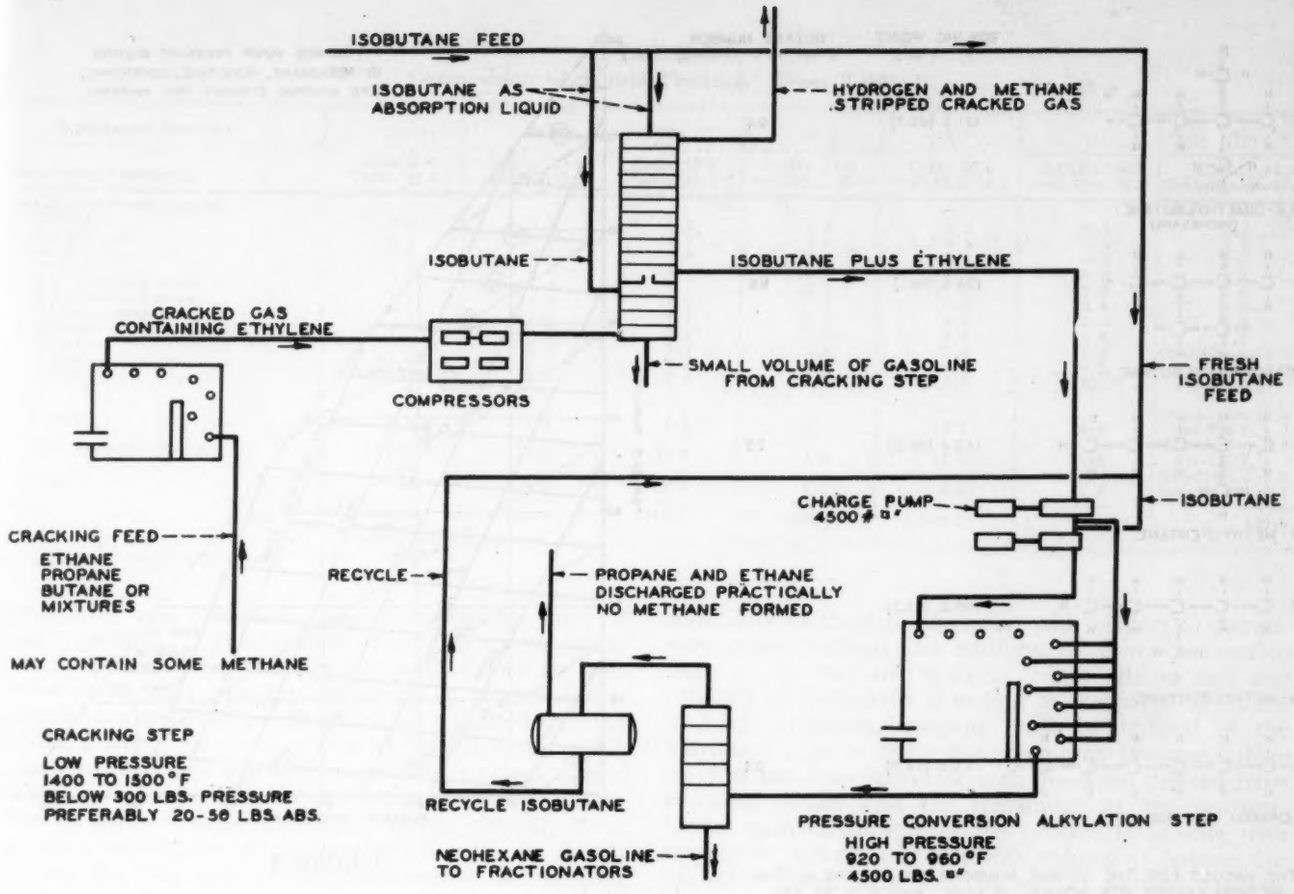

FIGURE 1
Neohexane Pilot Plant

usefulness of isomerization as another source of isoparaffins should not go unnoted.

Alkylation, furthermore, has a bearing on the utilization of hydrocarbon gas by conversion into motor fuel, in that the naturally occurring paraffin reactant is incorporated directly into the motor fuel molecule, and this makes for high yield and conserving of the combined hydrogen. Despite their greater abundance ethane and propane have been utilized hardly at all in gas polymerization in comparison with butane and refinery gas unsaturates. Processes proposed for ethane and propane generally require that they be cracked or dehydrogenated to olefins in one process step and the olefins polymerized in a second step, with the inherent expense of multistage operation. The use of alkylation in such a process means that a part of the paraffin reactant need not be subjected to the dehydrogenation step; some saving is effected in processing and the yield loss in dehydrogenation reduced. Contrasting alkylation so applied with catalytic polymerization, the latter as ordinarily practiced yields the less volatile gasoline hydrocarbons, while the former can be used when desired to produce the more volatile, as a means of volatility adjustment.

THERMAL ALKYLATION

The thermal alkylation reaction is brought about by subjecting a mixture of paraffins and olefins to a temperature bordering on the cracking range, approximately 950° F., at a high pressure, for example 3000-5000 pounds per square inch, the high pressure being required to reverse the cracking tendency. Olefins are readily polymerized by themselves under such conditions, but by maintaining the concentration of olefin low and paraffin high during reaction the polymerization is held back and the union of paraffin with olefin becomes the predominating reaction. This entails the addition of olefin during reaction at such a rate that its concentration never becomes too high. Sulfuric acid alkylation bears a general resemblance to thermal alkylation, except that the acid, acting as catalyst, brings about reaction at ordinary temperature and low pressures. The two types of alkylation are markedly different in the way different individual paraffins and olefins respond. As to the olefins, acid alkylation reacts isobutylene, n-butenes, and propylene readily, and ethylene with difficulty. Thermal alkylation on the contrary reacts isobutylene with difficulty, n-butenes and propylene more readily, and ethylene most readily of all. As to the paraffins, acid alkylation is selective and limited to isoparaffins, the simplest of which are isobutane and isopentane, while thermal alkylation reacts these isoparaffins and normal paraffins with equal ease, n-pentane and n-butane reacting readily as well as propane. Ethane and methane, however, react with difficulty. In its application to gas polymerization, thermal alkylation furnishes a route for converting ethane, propane and butane into motor fuel; ethane can be cracked or dehydrogenated to ethylene which can be used to alkylate propane and butane in a second step. Propane or butane can also serve as an olefin source through cracking or catalytic dehydrogenation.

By the selection of individual paraffins and olefins for thermal alkylation primary reaction products result from the union of one molecule of each, accompanied by secondary products. Ethylene and propane yield mainly isopentane, some n-pentane; ethylene and n-butane, 3-methyl pentane; ethylene and isobutane, neohexane;

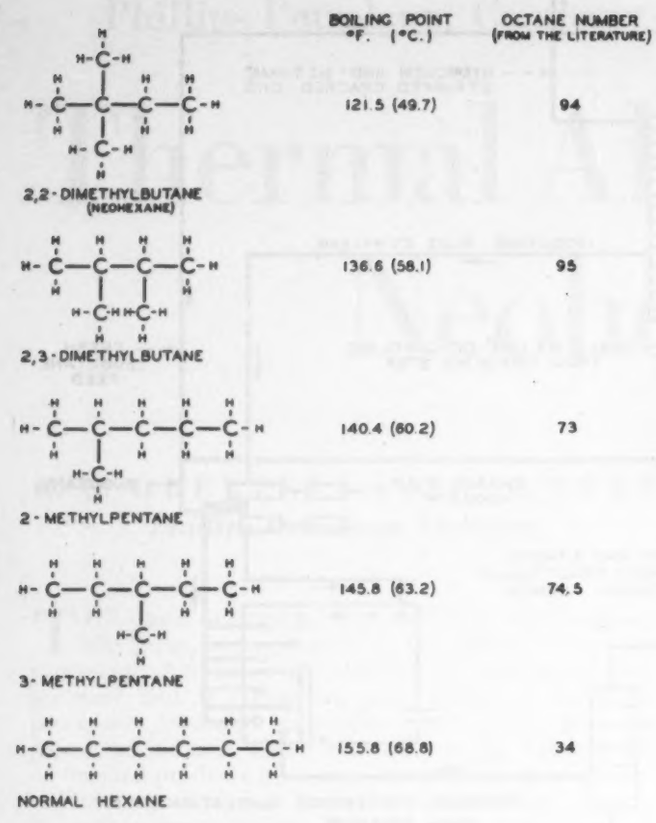

FIGURE 2

The Hexanes

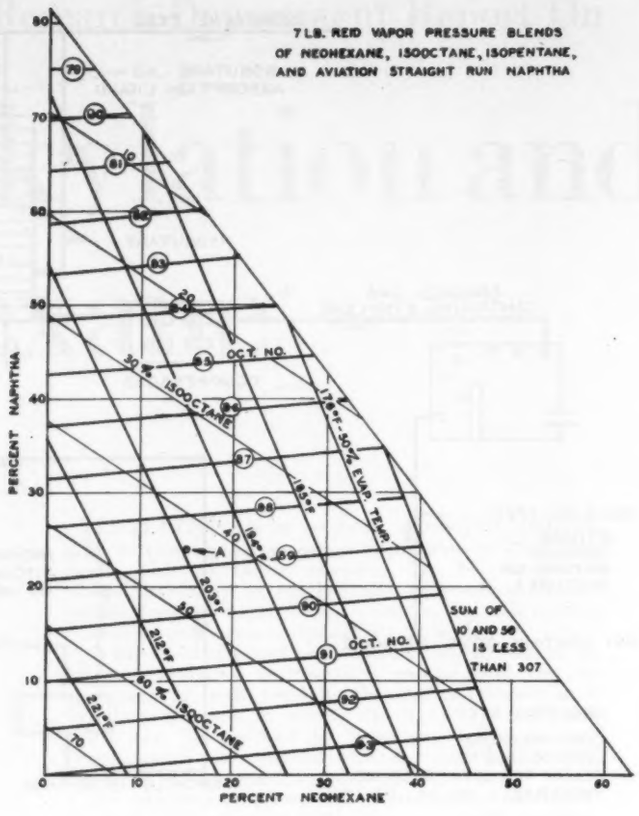

FIGURE 3

Anti-knock and Volatility Effect of Neohexane in High Octane Number Aviation Gasolines

TABLE 1

Products Formed by Interaction of Paraffins and Olefins Under Alkylation Conditions*

Experiment Number	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Reactants (Percent)	C_2H_4, 8.9 C_3H_8, 91.1	C_2H_4, 25 C_3H_8, 75	C_3H_6, 12.8 C_3H_8, 87.2	C_2H_4. 11.8 *iso*C_4H_{10}, 88.2	C_2H_4, 25.6 *iso*C_4H_{10}, 74.4	*iso*C_4H_8, 8.2 *iso*C_4H_{10}, 91.8	C_2H_4, 12.5 Cyclohexane 87.5
Pressure (lb./sq. in.)	4500	4500	6300	4500	4500	8000	4500
Temperature (°F. (°C.))	950(510)	950(510)	943(506)	959(515)	941(505)	907(486)	923(495)
Total reaction time, (minutes)	4.1	5.6	7.4	2.2	4	3.2	3.9
No. of olefin additions	20	10	10	14	10	10	10
Gasoline yield based on total products	11.2	32.8	20.5	14.8	35.4	2.9	22.5**
Analysis of products							
H_2	0.004	2.29	1.59	0.55	0.84	0.12	0.06
CH_4	0.716	2.29	1.59	0.55	0.84	0.12	0.06
C_2H_4	1.23	0.69	0.09	1.72	2.30	0.05	2.51
C_2H_6	0.53	4.10	2.64	0.71	1.44	0.04	0.37
C_3H_6	0.16	0.88	2.05	0.60	0.63	0.19	0.04
C_3H_8	84.40	54.17	69.29	0.76	2.04	0.05	0.04
isoC_4H_8	0.21	1.92	0.89	2.04	0.89	4.10	0.13
nC_4H_8	0.80	1.92	0.85	2.04	0.98	4.10	0.13
isoC_4H_{10}	0.70	3.17	2.09	78.77	56.37	92.36	0.38
nC_4H_{10}	0.70	3.17	2.09	78.77	56.37	92.36	0.38
C_5H_{10}	0.29	1.24	1.01	0.29	0.78	0.20	2.68
isoC_5H_{12}	6.20	9.38	1.36	0.73	1.11	0.11	2.68
nC_5H_{12}	1.82	4.22	1.79	0.73	0.97	0.11	2.68
C_6H_{12}	0.22	0.80	0.82	0.77	0.95	0.05	2.68
2, 2-Dimethylbutane	0.81	3.67	0.56	6.26	11.10	0.08	2.68
2, 3-Dimethylbutane	0.81	3.67	3.67	2.60	3.49	0.08	2.68
2-Methylpentane	0.81	3.67	3.54	2.60	3.49	0.08	2.68
n-Hexane	0.81	3.67	1.07	2.60	3.49	0.08	2.68
C_7H_{14}	0.20	0.76	0.54	0.36	0.71	0.10	Cyclohexane 73.96
C_7H_{16}	1.12	3.60	1.74	0.61	1.45	1.13	C_8 0.73
C_8H_{16}	0.12	0.62	0.50	0.47	1.03	1.01	Ethylcyclohexane 10.15
C_8H_{18}	0.37	2.95	1.23	1.89	4.84	1.05	284-356°F. (140-180°C.) 2.80
C_9+ to 392°F. (200°C.)	0.10	3 46	2.68	0.72	6.14	0.36	356-410°F. (180-210°C.) 4.07
	0.10		2.68			0.36	
Above 392°F.	0.10	3.08	2.68	0.15	2.83	0.36	Heavier 2.08
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* All percentages are by weight. ** Liquids other than cyclohexane.

TABLE 2
Composition of Liquid Products* From Table 1

Experiment Number	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Reactants (Percent)	C_2H_4, 8.9 C_3H_8, 91.1	C_2H_4, 25.0 C_3H_8, 75.0	C_3H_6, 12.8 C_3H_8, 87.2	C_2H_4, 11.8 *iso*C_4H_{10}, 88.2	C_2H_4, 25.6 *iso*C_4H_{10}, 74.4	*iso*C_4H_8, 8.2 *iso*C_4H_{10}, 91.8	C_2H_4, 12.5 Cyclohexane 87.5
Analysis of liquid products							
C_5H_{10}	2.6	3.7	5.1	1.9	2.2	6.5	2.8
isoC_5H_{12}	55.1	28.6	6.7	5.0	3.1	3.6	2.8
nC_5H_{12}	16.2	12.9	8.8	5.0	2.7	3.6	2.8
C_6H_{12}	1.9	2.4	4.4	5.2	2.7	1.6	2.8
2, 2-Dimethylbutane	7.1	11.2	2.7	42.1	31.3	2.6	2.8
2, 3-Dimethylbutane	7.1	11.2	18.0	17.5	9.9	2.6	2.8
2-Methylpentane	7.1	11.2	17.7	17.5	9.9	2.6	2.8
*n*Hexane	7.1	11.2	5.4	17.5	9.9	2.6	2.8
C_7H_{14}	1.8	2.3	2.4	2.4	2.0	3.2	Cyclohexane 76.7
C_7H_{16}	10.0	11.0	7.9	4.1	4.1	4.2	C_8 0.8.
C_8H_{16}	1.0	1.9	2 4	3.2	2.9	32.7	Ethyl-cyclohexane 10.5
C_8H_{18}	3.3	6.0	6.2	12.7	13.7	34.0	284-356°F. (140-180°C.) 2.9
C_9+ to 392°F. (200°C.)	1.0	10.6	12.3	4.8	17.4	11.6	356-410°F. (180-210°C.) 4.2
Heavier	1.0	9.4	12.3	1.1	8.0	11.6	Heavier 2.1
Total	100.00	100.0	100.0	100.0	100.0	100.0	100.0

* All percentages are by weight.

propylene and propane, 2,3-dimethylbutane and 2-methylpentane. Cycloparaffins react similarly, cyclohexane plus ethylene yielding ethylcyclohexane. In Table 1 are shown data from typical laboratory experiments in which various paraffin-olefin pairs were reacted together. Table 2 shows the composition of the alkylates. While catalytic alkylation often yields an isomer or rearranged form of the expected juncture product, thermal alkylation in many instances studied yielded primarily those products which can be represented on paper by merely joining the reactants without rearranging the resulting carbon skeleton.

It is noteworthy, for example, that ethylene and isobutane readily yield by thermal alkylation mainly neohexane (2,2-dimethylbutane) according to the reaction

$$CH_2=CH_2 + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3 \rightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_3$$

while catalytic alkylation has been reported to produce from these reactants 2,3-dimethylbutane, shown in Figure 2, to be later referred to.

In the synthesis of an individual hydrocarbon such as neohexane by the thermal alkylation process the olefin and paraffin feed stocks must be of rather high purity, the conversion per pass must be relatively low, and elaborate refining is needed for the finished products. In the manufacture of motor fuel by thermal alkylation an entirely different set of requirements prevails. In this broader and important application a considerably higher conversion per pass may be used, which permits greater output from the plant and produces an alkylate of lower volatility, such as is shown in Table 1, experiments (2) and (5).

The products do not reflect the reactants used to so great a degree, but light gas and tar formation remain low with consequent high gasoline yields relative to olefins and paraffins consumed. In combination with low pressure cracking as a source of olefins, thermal alkylation constitutes a variant on the familiar two-stage principle, characterized by high yields and much flexibility in the use of feed stock. Ethane, propane, and butane occur together in natural gas or refinery gas and where their value as gaseous fuel is not too high, they can be exhaustively recovered and converted to produce, in such a situation, the maximum volume of motor fuel by polymerization, by virtue of the non-selectivity of thermal alkylation with respect to conversion stock, without the addition of other conversion steps to the two-step process. Since ethane and also propane are ordinarily abundant as compared to butane in such situations, propane must be utilized in the alkylation step to make the volume of propane-butane more or less commensurate with the olefin derived from cracking ethane and the remainder of the propane. Under such circumstances the process is flexible with respect to reduction in available volume of butane. On the other hand, light straight run or natural gasoline hydrocarbons in the normally liquid range can be included to effect reduction in volatility when desired.

Finally, the alkylate resulting from such operations, being intended for motor fuel blending requires much less fractionation and refining.

Engineering and cost studies indicate that thermal alkylation in general compares favorably with thermal polymerization and is very definitely in the economic range for motor fuel entirely apart from the more dramatic role of synthesizing hydrocarbons of high purity.

NEOHEXANE PROCESS

By January, 1940, Phillips Petroleum Company will have in operation a plant for producing neohexane, a new aviation fuel ingredient, by the reaction of ethylene with isobutane by thermal alkylation. The process consists of a cracking step wherein an ethane-propane mixture is cracked to ethylene at low pressure and an alkylation step wherein the ethylene is reacted with isobutane under high pressure. The process is diagrammatically illustrated in Figure 1, which applies directly, however, to the pilot plant studies described below.

The thermal alkylation operation has been studied in a pilot plant wherein an ethane-propane mixture is cracked at about 1425° F. and a pressure a few pounds above atmospheric for optimum ethylene formation. The gaseous products are cooled, compressed, scrubbed with isobutane to remove light oils formed in cracking, and contacted with isobutane which absorbs the ethylene. The ethylene-isobutane mixture is pumped to a manifold which distributes it among 10 inlets situated along a tube coil which constitutes the reaction zone through which a separate stream of isobutane of greater volume is continuously pumped. A preheat coil imparts the desired reaction temperature, about 950° F., to the isobutane stream prior to its entry into the reaction zone, and this temperature, within the reaction zone, is main-

TABLE 3

Inspection Data on Products From Pilot Plant Alkylation of Isobutane by Ethylene

Sample Discription	A Debutanized Alkylate	B A Minus Neohexane Content	C* Neohexane Volatility	D** Plus Lower Fraction
Octane number (ASTM)..	82.5	78.4	100.2	99.6
API Gravity at 60°F.....	73.2	67.7	76.6	75.6
Reid vapor pressure lb. per sq. in.....	7.6	6.9	6.9	6.4
ASTM Distillation Percent evap. at °F.				
First drop.....	118	116	128	129
5.....	129	146	134	139
10.....	136	149	139	146
20.....	142	158	143	150
30.....	146	166	146	154
40.....	151	175	151	160
50.....	157	186	156	164
60.....	166	199	166	176
70.....	180	215	179	193
80.....	206	236	200	209
90.....	268	273	217	221
95.....	310	325	222	230
End point.....	370	399	258	282
Sum of 10+50% points.			295	310

* A blend of 40 volumes of acid treated C_7-C_8 fraction (165°F.-243°F.) with 60 volumes of neohexane fraction. Octane rating is by the ASTM method with 3 cc. TEL per gallon.

** A blend of 50 volumes of acid treated C_7-C_8 fraction (165°F.-243°F.) with 50 volumes of neohexane fraction. Octane rating is by the Army method with 3 cc. TEL per gallon.

tained by a flow of hot combustion gases. Conversion pressures are in the range 3000-5000 pounds per square inch. The liquid products are separated from the reactor effluent by conventional fractionation.

In addition to neohexane, other motor fuel hydrocarbons are produced, mainly through secondary reactions, and lying almost entirely above the neohexane in boiling range. Owing to the low maintained concentration of ethylene in the reaction zone, the formation of tar, usual in thermal polymerization, is retarded and the total alkylate is yellow in color, containing little material above the motor fuel range.

In Table 3 inspection data are shown for the total polymer (Sample A) after debutanizing and redistilling. After removing the neohexane from Sample A by fractionation and combining the lighter and heavier material, Sample B is obtained.

Sample C represents the product obtained by blending the neohexane fraction with a fraction including all the C_7 and C_8 material in the alkylate A, acid treated to eliminate unsaturates and redistilled. Such a blend is of interest in that it represents a 100 octane fuel of paraffinic type containing no isooctane. It meets specifications for aviation fuel in all respects except that the sum of the 10 + 50 ASTM distillation points is a little below the specified 307° F. minimum. Sample D represents a blend of slightly lower neohexane content which meets the sum specification as well.

NEOHEXANE

Neohexane is one of the five possible isomeric forms of hexane, all of which have been prepared synthetically.

TABLE 4

Boiling Points

Isopentane.....	82.3°F.	(27.95°C.)
*n*Pentane.....	96.8	(36.0)
Neohexane.....	121.5	(49.7)
2, 3-Dimethylbutane.....	136.6	(58.1)
2-Methylpentane.....	140.4	(60.2)
3-Methylpentane.....	145.8	(63.2)
*n*Hexane.....	155.8	(68.8)

The structural formulae and certain properties are shown in Figure 2. All but neohexane have been known for some years to occur in natural gasoline and only recently, in a West Virginia natural, was neohexane found.[18] An inspection of Figure 2 shows that only two of the hexanes, neohexane and 2,3-dimethylbutane, are highly branched in structure and possess high octane number, about 95 for each. As aviation fuels or fuel ingredients, these hydrocarbons are in the anti-knock range of synthetic isooctane, but by reason of their higher volatility can be used to provide volatility flexibly in blends of high anti-knock rating. Isoparaffins as a class are resistant to oxidation effects and consequently are advantageous under conditions requiring long intervals of storage.

Neohexane is the most volatile of the hexanes, and the boiling point, as it happens, is separated by considerable intervals from adjacent paraffins. This makes its manufacture in concentrated form by fractional distillation easy as will be evident from the following boiling point tabulation (Table 4).

There have been quite a few careful determinations of the physical properties of neohexane, which are in quite good agreement. The physical properties are listed in Table 5.

ANTI-KNOCK PROPERTIES

From an anti-knock viewpoint, a most important property of neohexane is its exceptionally high tetraethyl lead susceptibility. This quality is best demonstrated in Table 6, which shows the lead susceptibility of neohexane compared to that of a blend of the primary standards, isooctane and normal heptane, of the same unleaded octane number as neohexane.

It is of interest to note that at a TEL concentration of 3.0 cc. per gallon, neohexane is equal in anti-knock value to c.p. isooctane.

In view of the inherent limitations of the prevailing standard and official knock testing methods for testing fuels much in excess of 100 octane number, a good portion of the fundamental studies on the anti-knock properties of neohexane have been conducted, in our laboratories, on improved test methods. Perhaps the most interesting data of this nature obtained thus far are shown in Table 7. The anti-knock test method used for securing this information was the A.S.T.M. method with the following modifications: (1) removal of the throttle plate, (2) the use of a 10/16 inch venturi rather than the standard 9/16 inch venturi and (3) the spark advance held constant at 25° BTDC.

The superiority of neohexane to c.p. isooctane at comparatively high TEL concentrations is well demonstrated in the above tabulation. The blending effect of neohexane is shown in the third column of the table. Here it is shown that the high anti-knock value of leaded neohexane can be fully realized in blends of this material with isooctane.

VOLATILITY BLENDING RELATIONSHIPS

From a consideration of the volatility, anti-knock and TEL response properties of neohexane, it is apparent that the potential value of this new synthetic hydrocarbon lies chiefly in its use in raising the maximum attainable octane number of either ethylized or unethylized aviation fuels while at the same time maintaining fuel characteristics of balanced volatility. This is particularly true since it is a fact that synthetic isooctane has an average boiling point (220-240° F.) considerably in excess of the average boiling point (180-210° F.) of

the conventional aviation gasolines. From this consideration it is obvious that to obtain full advantage of the superior anti-knock properties of synthetic isooctane it is desirable to have a blending material of considerably lower average boiling point but with superior anti-knock properties. Neohexane with an average boiling point of 121° F. and an octane number of 94 fills this need.

Table 8 presents the A.S.T.M. distillation data for a series of blends of neohexane, commercial isooctane, aviation straight run naphtha, and isopentane. The characteristics of the base materials are presented in the table. The commercial isooctane was composed largely of the synthetic higher boiling isooctanes. The aviation straight run naphtha was a depentanized straight run aviation gasoline of the usual conventional volatility characteristics. The neohexane and isopentane were of high purity.

In these blending experiments the naphtha and the isooctane were "isopentanized" and the isooctane was "neohexanized" to 5.5, 7.0 and 8.5 pounds, giving three base materials in each vapor pressure bracket for cross blending. The three blends in each vapor pressure bracket were blended in pairs with each other in 1/3 and 2/3 proportions. The composition, A.S.T.M. distillation data, and vapor pressure data are presented in Table 8.

In addition, octane numbers, calculated arithmetically from the composition and the octane numbers assumed as representative for the basic ingredients, are shown in the table. These octane numbers are, of course, for illustrative purposes only but will permit the establishment of a semi-quantitative relationship between volatility and anti-knock properties. In connection with these anti-knock relationships it should be mentioned that the aviation naphthas quite generally have basic lead susceptibilities inferior to those possessed by isopentane, neohexane and commercial isooctane. Since the octane numbers of these blends are almost directly related to the percentage of naphtha in them—the higher the percentage, the lower the octane number—it follows that the basic TEL susceptibility of the blends will be higher, the higher the octane number of the blend.

Table 8 is divided into four sections, the top section of four items dealing with the four basic ingredients. The remaining three sections deal with blends in the three vapor pressure brackets, 5.5, 7.0 and 8.5 pounds, respectively. In each of the vapor pressure brackets the blends are arranged in order of decreasing naphtha content. For all but the highest naphtha concentration in each vapor pressure bracket there are examples of blending with and without neohexane.

As would be expected from the inspection data on the four blending ingredients, the blends meet conventional aviation gasoline volatility specifications through most of the blending range. All the blends meet the conventional 10 and 90 percent specifications, while in certain very limited blending proportions the blends have too little or too much volatility to meet the conventional volatility specifications.

The 7.0 pound blends are, of course, of most immediate significance, although it is of interest to know that some of the 8.5 pound blends have higher average boiling points than some of the 5.5 pound blends. With the data pertaining to the 7.0 pound blends as a basis, Figure 3 has been prepared. The percentages of naphtha and of neohexane are the coordinates in the figure. In light lines are shown the percentages of isooctane. The percentage of isopentane at any point in the diagram is,

TABLE 5
Properties of Neohexane

Reid vapor pressure, lb.	5.9
A. P. I. Gravity	84.9
ASTM octane number	94
Boiling point, °F.(°C.)	121.5(49.7)
Specific gravity (20°C./4°C.)	0.6494
Refractive index n_D 20°C.	1.36887
Freezing point (°F.)-(°C.)	-144.8 (-98.2)

TABLE 6
Lead Susceptibility of Neohexane and Isooctane

	Octane Number (ASTM Method)	TEL Requirements to Equal C.P. *Iso*octane Plus Indicated TEL (AS TM Method)			
		0.0 cc.	1.0 cc.	2.0 cc.	3.0 cc.
Neohexane (99 percent pure)	94	0.25	1.35	2.25	3.0
*Iso*octane-Normal Heptane blend	94	0.30	2.90	4.85	6.35

TABLE 7
Knock Test by Modified A.S.T.M. Method

Octane* Number	cc. TEL per gallon C.P. *Iso*octane	TEL Required to Equal Leaded *Iso*octane		
		Neohexane	50% Neohexane + 50% C.P. *Iso*octane	39% *Iso*pentane + 61% C.P. *Iso*octane
100	0.0	0.25	0.1	0.25
109.1	1.0	1.3	1.1	1.5
112.1	2.0	2.2	2.1	2.6
114.1	3.0	2.9	2.9	3.75
118.7	6.0	4.5	4.9	7.45
–	9.7	6.0	—	—

* Reference (10).

TABLE 8
Inspection Data on Neohexane Blends

Percentage Composition				ASTM Distillation Data Temp. (°F.) at indicated percent Evaporated						Octane No. (1)	R.V.P. (lbs.)
Naphtha	*Iso*-octane	*Neo*-hexane	*Iso*-pentane	10	30	50	70	90	10+50		
100	....	....	....	176	188	202	219	247	378	75.0(2)	3.65
....	100	....	....	225	230	234	240	263	459	94.0(2)	1.40
....	....	100	....	120	120	121	121	122	241	94.0(2)	9.85
....	....	....	100	82	82	82	82	82	164	90.0(2)	21.00
90.5	....	....	9.5	155	179	197	215	243	352	76.4	5.5
60.3	27.2	....	12.5	157	187	209	225	250	366	82.0	5.5
60.3	18.4	15.0	6.3	154	174	196	219	247	350	82.3	5.5
30.2	54.3	....	15.5	157	197	220	234	256	377	87.5	5.5
30.2	36.7	30.0	3.1	151	166	193	224	248	344	88.1	5.5
....	81.5	....	18.5	158	210	230	238	258	388	93.3	5.5
....	72.7	15.0	12.3	155	193	224	236	257	379	93.5	5.5
....	63.8	30.0	6.2	152	175	210	234	254	362	93.8	5.5
....	55.0	45.0	....	148	162	190	227	251	338	94.0	5.5
81.5	....	....	18.5	139	162	189	212	241	328	77.8	7.0
54.4	24.8	....	20.8	139	170	203	223	247	342	82.8	7.0
54.4	12.3	21.0	12.3	139	156	179	212	242	318	83.2	7.0
27.2	49.7	....	23.1	138	178	216	232	253	354	87.8	7.0
27.2	24.7	42.0	6.1	137	149	165	204	243	302	88.6	7.0
....	74.5	....	25.5	138	191	226	237	256	364	93.0	7.0
....	62.0	21.0	17.0	137	166	209	234	253	346	93.3	7.0
....	49.5	42.0	8.5	137	152	181	225	250	318	93.7	7.0
....	37.0	63.0	....	134	141	155	191	245	289	94.0	7.0
72.5	....	....	27.5	127	148	177	207	237	304	79.1	8.5
48.3	22.7	....	29.0	128	153	193	220	247	321	83.7	8.5
48.3	6.3	27.0	18.4	127	140	160	194	237	287	84.1	8.5
24.2	45.3	....	30.5	128	161	209	229	252	337	88.2	8.5
24.2	12.7	54.0	9.1	126	134	145	167	234	271	89.0	8.5
....	68.0	....	32.0	128	168	223	236	255	351	92.7	8.5
....	51.7	27.0	21.3	127	146	181	227	250	308	93.1	8.5
....	35.3	54.0	10.7	126	135	150	190	243	276	93.6	8.5
....	19.0	81.0	....	126	130	135	147	224	261	94.0	8.5

NOTES: (1) Calculated arithmetically from octane numbers of ingredients.
(2) Assumed as representative.

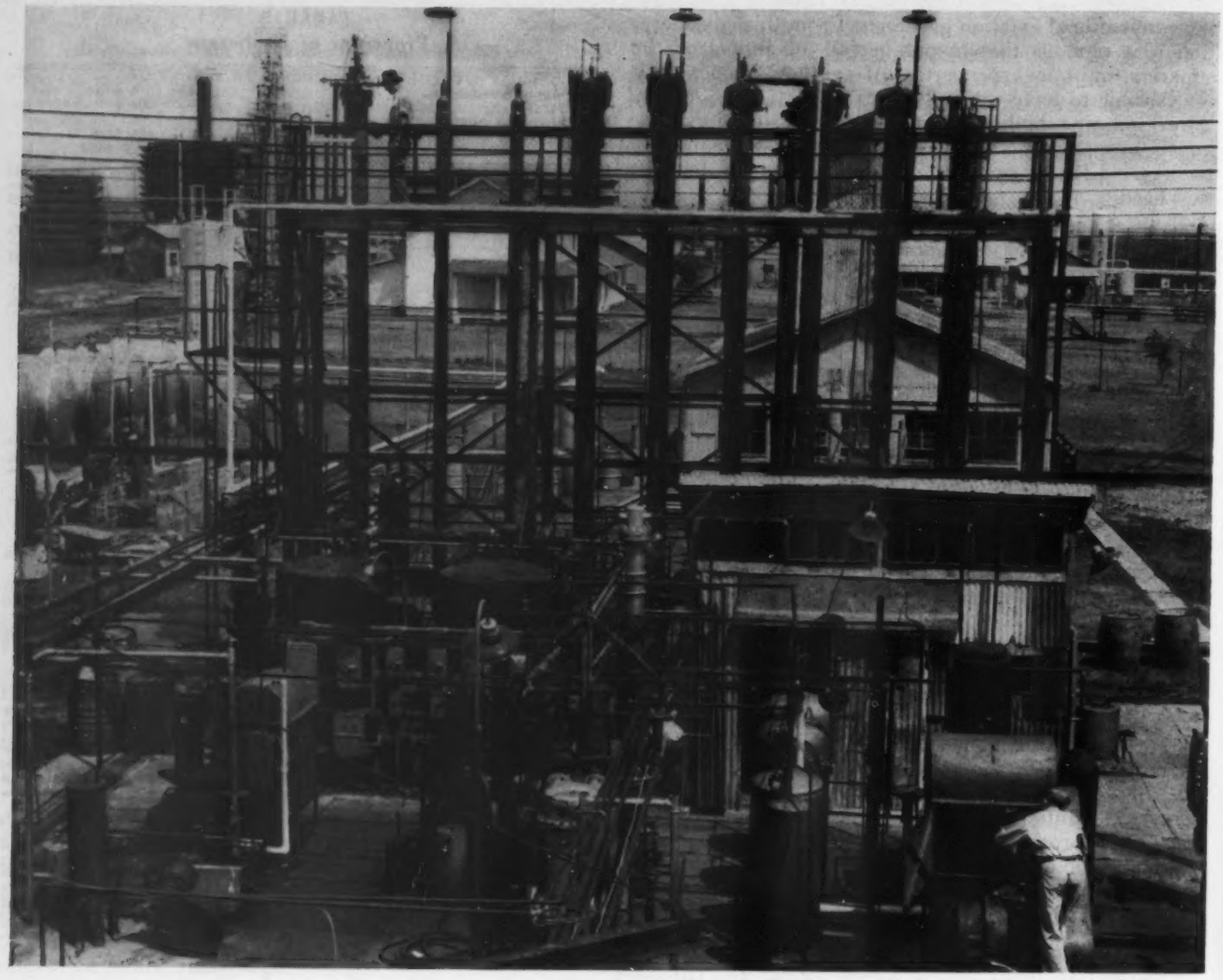

FIGURE 4
Neohexane Pilot Plant

of course, the difference needed to total 100 percent. All points in the triangular diagram represent a total composition of 100 percent. Thus the upper apex of the triangle is a blend containing 81.5 percent naphtha and 18.5 percent isopentane, the lower left apex is a blend containing 74.5 percent isooctane and 25.5 percent of isopentane, and the lower right apex is a blend containing 63 percent neohexane and 37 percent isooctane. The vertical axis represents the condition of conventional blending to high octane numbers using isooctane, aviation naphtha, and isopentane. The horizontal axis represents blends using neohexane, isopentane and isooctane but containing none of the low octane number aviation naphtha. All points in the body of the diagram represent combinations of these two blending practices, using all four ingredients.

Sloping sharply downward is a family of curves (dark lines) showing the 50 percent temperatures of the blends. The extreme right line parallel to the 50 percent temperature lines represents the dividing line between blends with more and less than 307° F. for the sums of the 10 and 50 percent temperatures; all blends to the left of the line having sums of more than 307° F. Sloping slightly upward from left to right is another family of curves (dark lines) showing the unleaded octane numbers of the blends.

As an example of the use of Figure 3, the point designated as A has the following composition:

Percent neohexane .. 15.0 (horizontal axis)
Percent naphtha ..... 25.0 (vertical axis)
Percent isooctane .... 43.3 (interpolation between 40 and 50 lines)
Percent isopentane ... 16.7 (by difference)

and the following definite characteristics:

Unleaded octane number—88.4 (interpolation between 88 and 89 lines)
50% Evap. temperature—202° F. (interpolation between 194 and 203 lines)
Sum of 10 and 50% temperatures—More than 307° F. (left of 307 boundary)
Reid vapor pressure—7.0 pounds (basic premise)

and the following approximate characteristics from the data on 7.0 pound blends in Table 8:

10% evaporated temperature—134-139° F.
90% evaporated temperature—241-256° F.

The figure graphically shows the advantage of neohexane in making it possible to have higher octane number gasolines with balanced volatility. Thus, for any given midpoint limitation it is possible to make finished gasolines of considerably higher octane numbers when

neohexane is used to the maximum extent. For a midpoint maximum of 212° F., the maximum attainable clear octane number without neohexane is 86.2, while replacing the naphtha with a mixture of neohexane and additional isooctane makes it possible to get to 93.3 octane number, a gain of 7.1 octane numbers. Under similar conditions, but for a midpoint maximum of 203° F., the gain is 10.6 octane numbers, from 82.8 to 93.4. For higher and lower midpoint maxima the gains are less and more, respectively. The improved basic TEL susceptibility of these higher octane number gasolines, previously mentioned, is of considerable value in the case of ethylized gasolines.

From studies of the literature pertaining to the vaporization characteristics in actual engine induction systems and from a considerable experience in blending materials of widely divergent average boiling points there can be little question as to the practical vaporization characteristics of the blends shown in Table 8 and Figure 3. However, the question will naturally arise in many minds as to the practical vaporization characteristics of such fuels as are represented by the horizontal axis of Figure 3. These fuels are essentially three component mixtures with considerable differences among the boiling points of the individual components. As is shown in Figure 3, the A.S.T.M. distillation points in almost all the blending range are well within conventional limits. But the question is whether the A.S.T.M. distillation data can be expected to give the established relationship to actual vaporization in an engine manifold in the case of such three component mixtures. In this connection it is to be recalled that much work[1,2,3] has been done relating the laboratory Sligh air-equilibrium distillation data to A.S.T.M. distillation data and to engine performance. In particular, Brown[3] studied motor fuels having far wider variations in the A.S.T.M. distillation curves than are encountered in isopentane-neohexane-isooctane blends. However, it has seemed desirable to conduct both Sligh air-equilibrium tests and engine tests on the neohexane blends to determine if there are any unexpected vaporization characteristics. This work is now in progress, but is too incomplete to be discussed here in detail except to state that thus far there has been a reasonably good agreement between the actually determined air-equilibrium distillation curves and the air-equilibrium distillation curves that would have been predicted from the relationships established by the earlier investigators. This fact would indicate that the conventional volatility specifications will be applicable to even the three component blends.

(*Continued on page* 125)

FIGURE 5
Phillips Petroleum Company Refinery at Borger, Texas

High-Octane Aviation Fuel

By the Sulfuric-Acid Alkylation Process

A Contribution by

Anglo-Iranian Oil Company, Ltd., Humble Oil and Refining Company, Shell Development Company, Standard Oil Development Company, and The Texas Company

Read by K. G. Mackenzie

AVIATION fuels with octane ratings approaching 100, or above, are increased greatly in commercial availability by the introduction of the sulfuric-acid alkylation process.

This process affects directly the union of *iso*paraffins with olefins in approximately equal volumes to form branched-chain paraffins in the presence of strong commercial sulfuric acid as the catalyst, and in a single-stage operation.

A new source of high-octane gasoline is available; and, with sufficient *iso*paraffin, potential yields of branched-chain product by alkylation from a given refinery stream are more than double those obtainable by the two-stage process of olefin polymerization followed by hydrogenation.

Standard materials of construction are used in the six alkylation plants now in operation and the others under construction. The catalyst is of universal availability; and, after use in the process, may be re-used in treating operations, or may be recovered by conventional methods.

The alkylation process is unusually well adapted to commercial application, and marks an important step forward in both the petroleum and aviation fields.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

BRANCHED-CHAIN paraffins are outstandingly valuable as aviation fuels,[1] as is evidenced by the increase in their consumption for making 100-octane gasoline. In 1937 the domestic consumption of 100-octane aviation fuel was approximately 7,000,000 gal., and it has been estimated this increased to 20,000,000 gal. in 1938.[2] The anticipated consumptions for 1939 and 1940 are greatly in excess of these figures; and, with the assurance of a larger supply of 100-octane fuel at a reasonable price, a further increase undoubtedly will result from changes in airplane-motor design to take advantage of the better performance and economy possible when operating with such a gasoline.

The normally gaseous hydrocarbons such as C_3 and C_4, because of their high volatility, find only a limited use in gasoline; but they are capable of being transformed into high-octane fuels of very great value. Processes in which the lower olefins from cracking operations first are polymerized and then hydrogenated are in successful operation already, and have been described in the literature.[3] Another method of utilizing the light hydrocarbons exists in which the paraffin is combined directly with the olefin to produce a saturated fuel, thus avoiding the two stages of polymerization and hydrogenation. Previous investigations have shown that metallic halides, such as aluminum chloride and boron trifluoride, catalyze the reaction of *iso*paraffins with olefins. This coupling reaction usually is designated as an alkylation reaction. However, alkylation using metallic halides as catalysts as yet has not been developed to a commercial process.

Recently it has been shown that sulfuric acid is a catalyst for the reaction. The rapid development of the commercial process has depended upon the use of this catalyst, as it provides a cheap material which can be handled in standard engineering equipment under conditions similar to those existing in proven processes. The products obtained have a high octane number, and possess the other characteristics necessary for superior aviation fuels.

The present sulfuric-acid process represents the combined efforts of the Anglo-Iranian, Humble Oil, Shell Development, Standard Oil Development, and Texas research staffs. These groups, working independently, had developed processes which, though somewhat different in details of operation and in the results obtained, were in principle essentially similar. In the best interest of the petroleum industry as a whole, and in order that a major new source of high-octane aviation fuel should be made available for national defense without delay or waste of correlative experience, their efforts recently have been combined to expedite the commercial application of the process.

It is not the intention of the present paper to review in detail the theory of the alkylation reaction nor its possible widespread application in organic chemistry. Data of this type have been reported already at recent scientific meetings[4] and in the literature.[5] Rather, it is intended to outline briefly the underlying principles; and then discuss the type of equipment used, the conditions of operation, and the results which can be obtained when operating with various representative feed stocks.

PRINCIPLES OF OPERATION

When aliphatic olefins are mixed with strong sulfuric acid at around atmospheric temperatures, the primary reaction is one of olefin absorption in the acid to form alkyl sulfates. This absorption is a relatively rapid exothermic reaction. Saturated normal

hydrocarbons remain virtually unabsorbed, but *iso*paraffins such as *iso*butane are absorbed to a slight extent if the sulfuric acid is at a concentration of 90 percent or higher. It has been estimated that the rate of absorption of the olefins is about 700 times faster than that of the *iso*paraffins.

Although it is not necessary for our purpose to assume a particular reaction mechanism, it is helpful to visualize that the coupling reaction occurs in the acid phase through the formation of an olefin acid ester, which then reacts with the *iso*butane. In simple form, the reaction would consist of the following two steps:

Absorption Step

$$CH_3CH_2CH{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2CH(HSO_4)CH_3$$

Butylene—1 + Acid → Alkyl ester

Coupling Step

$$CH_3CH_2CH(HSO_4)CH_3 + (CH_3)_2CH-CH_3 \longrightarrow CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + H_2SO_4$$

Alkyl ester + *Iso*butane → Octane + Acid

Actually, the reaction is considerably more complicated, as the product first formed tends to undergo splitting and rearrangement. Other explanations involving, for example, assumptions of hydrogen-ion exchange are also capable of accounting for the reactions which occur; but it is not our intention to discuss these points at this time—which, in any case, have little bearing on process operations.

In order to prevent the absorption step from proceeding to a point where the acid becomes useless for coupling, it is desirable to have present in the reaction zone a vast excess of *iso*paraffin. In batch studies, this mass effect of the *iso*paraffin is achieved by adding slowly the olefin to an emulsion of the *iso*paraffin and sulfuric acid. When the rate of addition is kept sufficiently slow to prevent any accumulation of unreacted olefin in the reactor, a completely-saturated product is obtained. However, much faster overall reaction rates and better control of the reaction can be obtained by continuous operation.

In continuous operation, the suppression of the extent of olefin absorption is achieved first by diluting the olefin feed with *iso*paraffins, and then adding this mixture to an emulsion of acid and reacted hydrocarbon which is rich in *iso*paraffins, but substantially olefin-free. In commercial plants, the requisite mixing is obtained by the use of a circulating pump and additional reaction space in which intimate contact is maintained by the velocity of flow through baffles or jets. A simplified flow diagram of a commercial plant is given in Fig. 1.

Modifications of these single-stage reactors, of course, are possible, and in certain instances may lead to improved results. Additional reactors may be arranged in parallel or in series, and the feed may be split between the reactors.

Sulfuric acid is the only chemical agent used, although a caustic wash of the product usually is provided to neutralize any traces of acid which might be carried over from the separator to the fractionation system. In commercial operation, a portion of the acid continuously is withdrawn from the separator, and replaced by makeup acid of 96- to 100-percent strength. This replacement is essential if the quality of the product is to be maintained, as otherwise side reactions gradually would weaken the acid to a point where it no longer efficiently could catalyze the alkylation reaction. The acid usually is withdrawn at from 88- to 90-percent titratable acidity, but other ranges in certain instances may apply—depending on the feed stocks being processed and the quality of product desired. The drop in acidity from 98 to 90 percent, or lower, is due largely to the absorption of hydrocarbons in the acid—although contamination by products from oxidation and other side reactions are contributing factors. This dilution effect is by no means equivalent to water dilution, because 90-percent sulfuric acid, in which water makes up the other 10 percent, is entirely unsuitable for alkylation.

The amount of acid added usually is referred to as acid replacement, and is a major factor in determining the efficiency of operation. The quantity added is affected both by the composition of the feed stocks and by the operating conditions used. Strictly speaking, the acid is not consumed in the chemical sense, but merely is diluted by the hydrocarbon. A major part of the acid can be recovered by conventional reconcentration methods, or it can be used for acid treating elsewhere in the refinery.

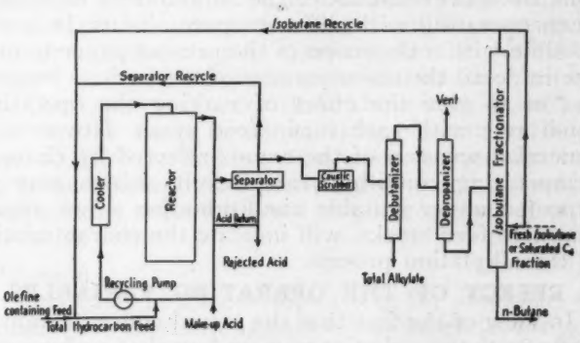

FIGURE 1
Flow Diagram—Sulfuric-Acid Alkylation Plant

FEED STOCKS

Alkylation can be carried out with a wide variety of olefins and *iso*paraffins, but for all practical purposes olefins from C_3-C_8, inclusive; and the *iso*paraffins, *iso*butane and *iso*pentane, are those used. Ethylene-containing feed stocks may be used, but the reaction is accompanied by an increased acid consumption. Olefins above C_8 yield products boiling largely above the aviation-gasoline range. However, it has been found that some C_4 and C_3 polymers containing eight or more carbon atoms prepared by catalytic process and some other olefins of branched structure rearrange on alkylation to yield products boiling below those expected, and predominantly in the gasoline range.[4]

*Iso*butane is the most-widely used *iso*paraffin; because, on account of its high volatility, it has a restricted direct use in gasoline. When coupled with olefins, it leads to products having a highly-branched structure. *Iso*pentane and *iso*hexane are in themselves valuable constituents of gasoline, and would

be used only in the alkylation process if large quantities were available over and above those required to meet volatility requirements.

*Iso*butane is alkylated readily by most of the pure olefins, and with a low catalyst consumption. Unfortunately, in the refinery the olefins are present in mixtures along with dienes, aromatics, mercaptans, thiophenes, and other substances. These may affect markedly the yield and acid consumption; as in the laboratory it has been shown that mercaptans, amines, dienes, aromatics, and oxygenated compounds are absorbed by the acid, and reduce its activity rapidly. The cost of pretreating the feed to remove these impurities must be weighed against the resulting economy in acid. For example, the oxidation of the sulfur compounds causes an increase in consumption of acid, but does not affect directly the quality of the product. A simple, caustic wash, therefore, usually is warranted. Amines, if present, can be removed by water washing. Dienes,* aromatics, and oxygenated compounds, however, are more difficult to remove; and it is doubtful if a pretreatment process is justified. Entrained water is removed by settling, but the quantity of dissolved water present hardly justifies much expense in predrying the feed. Thus, each feed stock constitutes a separate problem depending on the amount and type of impurity present, and may require adjustment of the operating conditions over and above the adjustments necessary when operating with different pure olefins. It is not possible within the scope of the present paper to outline in detail the consequences of the various impurities or to give the effect of varying the operating conditions with each olefin feed stock. However, a general discussion of the trends affected by changes in operating conditions, and results which may be expected under suitable conditions for a few representative feed stocks, will indicate the characteristics of the alkylation process.

EFFECT OF THE OPERATING VARIABLES

In view of the fact that the actual concentration of olefin in the reaction zone is so low that under practical operating conditions it cannot be measured, it is necessary to consider the alkylation reaction from a study of the variables enumerated below:

*Iso*paraffin-olefin ratio
Contact time
Acid strength
Temperature
Acid-hydrocarbon ratio
Olefin concentration of the feed
Agitation

In the consideration of the effects of these variables, it should be kept in mind that they are all interdependent and that, fortunately, factors which increase the acid life also improve the yield and quality of products.

Iso*paraffin-Olefin Ratio*

The *iso*paraffin-olefin mole ratio in the hydrocarbon feed stock prior to contact with acid is an extremely important variable, and has a marked influence on the acid life and on the yield and quality of product. In accordance with the concept of mass action, the higher the ratio, the better the results obtained. This is shown in the case of an *iso*butane-C_4 olefin feed in Fig. 2; the other operating conditions were constant for this series of experiments. It will be seen that there is a marked increase in the total yield, percent of aviation fraction, and octane number of the product, and a corresponding decrease in the acid consumption, as the *iso*paraffin-olefin ratio is increased from 2:1 to 5:1. A 5:1 ratio, therefore, usually is chosen as the lowest ratio for commercial operation with C_4 olefins. A similar effect is noted with other olefinic feed stocks. With C_5 and the higher olefins which appear to be somewhat less reactive, ratios greater than 5:1 normally are used.

These high ratios are obtained by blending the olefin feed and the required makeup *iso*butane with *iso*butane recovered from the fractionation system. Alternatively, in order to reduce the fractionation load, the hydrocarbon phase which is rich in *iso*paraffin may be recycled from the top of the separator to meet the feed prior to its contact with the acid—thus increasing an original *iso*butane-olefin ratio of less than 5:1 to 5:1 or greater.

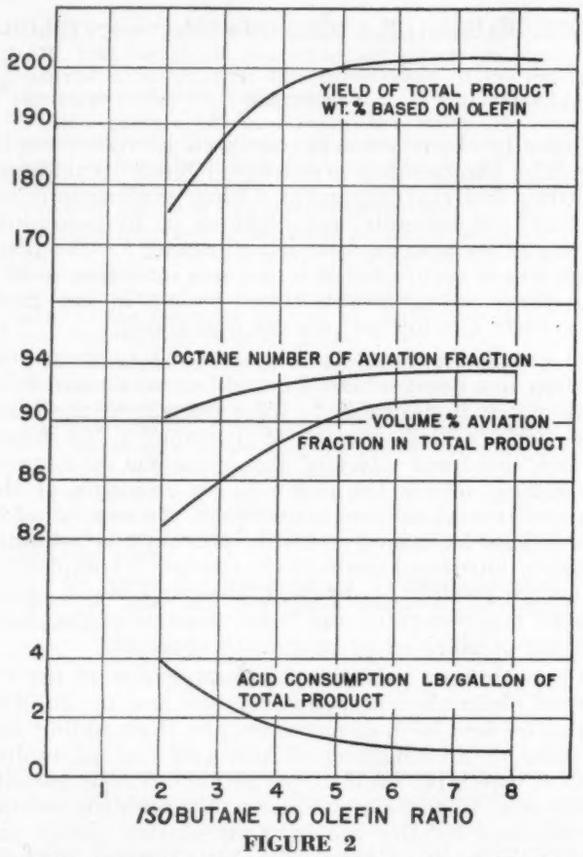

FIGURE 2

Effect of* Isobutane to Olefin Ratio *for* C_4 *Olefins

Another alternative is to use several stages in series, and split the olefin feed between the stages. This is done by adding the olefin to the hydrocarbon phase from each separator before it enters the succeeding stage. A simplified flow diagram showing this variation is given in Fig. 3. It will be seen that in a large commercial plant where several parallel reactors are already available, this splitting of the olefin feed very easily is carried out by relatively-minor piping changes, and many of the plants now under construction have provisions for both separator recycle and split-olefin feed.

However, neither of these two alternatives is equivalent to returning the same amount of pure *iso*butane, as it has been found that side reactions are enhanced by the higher concentration of product and

* Butadiene will alkylate to give principally octanes, but the acid consumption is high.

its prolonged contact in the reaction zone. These alternatives do give a substantial reduction in the amount of *iso*butane recycle; and provide a means for further improving the yield, acid life, and quality of product in a system which already has a relatively-high *iso*butane-olefin ratio obtained in the normal manner.

Although the ratio of *iso*butane to olefin in the feed to the reactor is very high, the actual consumption of *iso*butane is about theoretical (i.e., one mole of *iso*-paraffin to one mole of olefin), and can be slightly in excess due to splitting of the saturated product to a saturated hydrocarbon and an olefin, which latter can react with more *iso*butane; thus, yields in excess of theoretical actually are obtained in certain instances. As there is a deficiency of *iso*butane relative to olefins in most refinery C_4 feed stocks, an additional supply of *iso*butane is required. The availability of *iso*butane, therefore, becomes the basis for determining the size of an alkylation plant and the feed stock to be used; processes for the isomerization of normal butane to *iso*butane are clearly of interest here.

Contact Time

The contact time usually is expressed by the ratio of the volume of hydrocarbon phase in the reaction zone to the volume of hydrocarbon feed per unit of time. From batch data it might appear that long contact times would be required for this reaction. Actually the reaction is quite fast, and high production rates are attained in the reaction systems developed. Contact times as low as 5 minutes have been used with C_4 fractions, although 20 minutes to 40 minutes have been allowed in the design of commercial plants. It is difficult to give an optimum contact time for

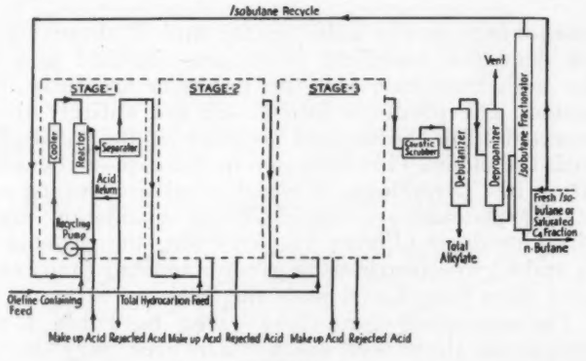

FIGURE 3

Flow Diagram—Three-Stage Sulfuric-Acid Alkylation Plant, Split-Olefin Feed.

all feed stocks. With butylene feed stocks, the effect of reducing the contact time to less than 5 minutes is to reduce the quality of the product, and increase the concentration of olefin absorbed in the acid. With some other feed stocks, this effect is more pronounced at longer contact times.

Acid Strength

The acid strength is an extremely important variable, and there is a great difference between the makeup acid strength and the actual acid strength in the reactor. It has been found that the practical makeup acid strength lies between 96 and 100 percent acid. Lower acid strengths are somewhat more effective at higher temperatures, whereas 98- to 100-percent acids are best below 70° F. The acid strength in the reactor proper is lower than the makeup acid strength due to the accumulation of the hydrocarbons and some water which is introduced in the feed stock, or is derived from side reactions such as oxidation of the products. Under usual operating conditions, the acid in the reactor has a titratable acidity of 88 to 90 percent, and is maintained at this strength by the addition of makeup acid.

Temperature

The effect of temperature closely is associated with acid strength, and differs with different olefin feed stocks. Makeup acid of 98- to 100-percent strength, when used much above 70° F., leads to increasing oxidation of the hydrocarbons—which results in increased acid replacement, and decreased yield and quality of products. With C_4 olefins, lower temperatures appear to favor catalyst life, and the optimum temperature in this case lies between 32 and 50° F.

Acid-Hydrocarbon Ratio

The volume ratio of acid to hydrocarbon in the reaction zone is also important. For most purposes, this is about 1:1; but in specific instances it may be as high as 2:1. Variations within this range are not critical, but higher or lower ratios give poorer results.

Olefin Concentration of the Feed

The effect of olefin concentration in the total hydrocarbon feed is of secondary importance, provided the *iso*butane-olefin ratio is maintained. In order to reduce equipment sizes and the acid consumption as much as possible, it is desirable to have the olefin concentration reasonably high. With average C_4 fractions from cracked gasoline as the olefin feed stocks, and with a 5:1 *iso*butane-olefin ratio, the olefin concentration will vary from about 8 to 14 percent, and in this range about equal results are to be expected. The normal paraffin present does not enter into the alkylation reaction; but if present to a large extent, may require a small increase in the *iso*paraffin to olefin ratio.

Agitation

Very early in the development of the process it was found that excellent agitation was essential for good results. In experiments in which poor dispersion was used, low yields of product resulted, and the acid consumption was high. Many means for obtaining a good dispersion were studied. These included various mechanically-driven mixers, packed towers, and combinations of pumps with jets or baffles. However, it soon was found that intimate contact best was obtained by means of a pump-recycling-acid-hydrocarbon emulsion through a system of jets or baffles. This method, therefore, has been adopted uniformly for commercial installations.

CHARACTERISTICS OF PRODUCTS

The products are particularly suitable as aviation fuels because of their *iso*paraffinic nature, high octane number, high lead susceptibility, very low sulfur content, high calorific value, and lack of sensitivity to different engine conditions.

With the exception of the alkylation product from a gasoline of 210°F. end point, products of *iso*butane and the lower olefins boil almost entirely in the gasoline range; from 85 to 90 percent boils below 300°F. Thus they are an excellent source of blending materials for aviation gasolines.

It has been pointed out that, although the alkylation reaction can be applied to a wide variety of olefin feeds, the conditions of operation for these feeds may differ. This is particularly true of the cracked-

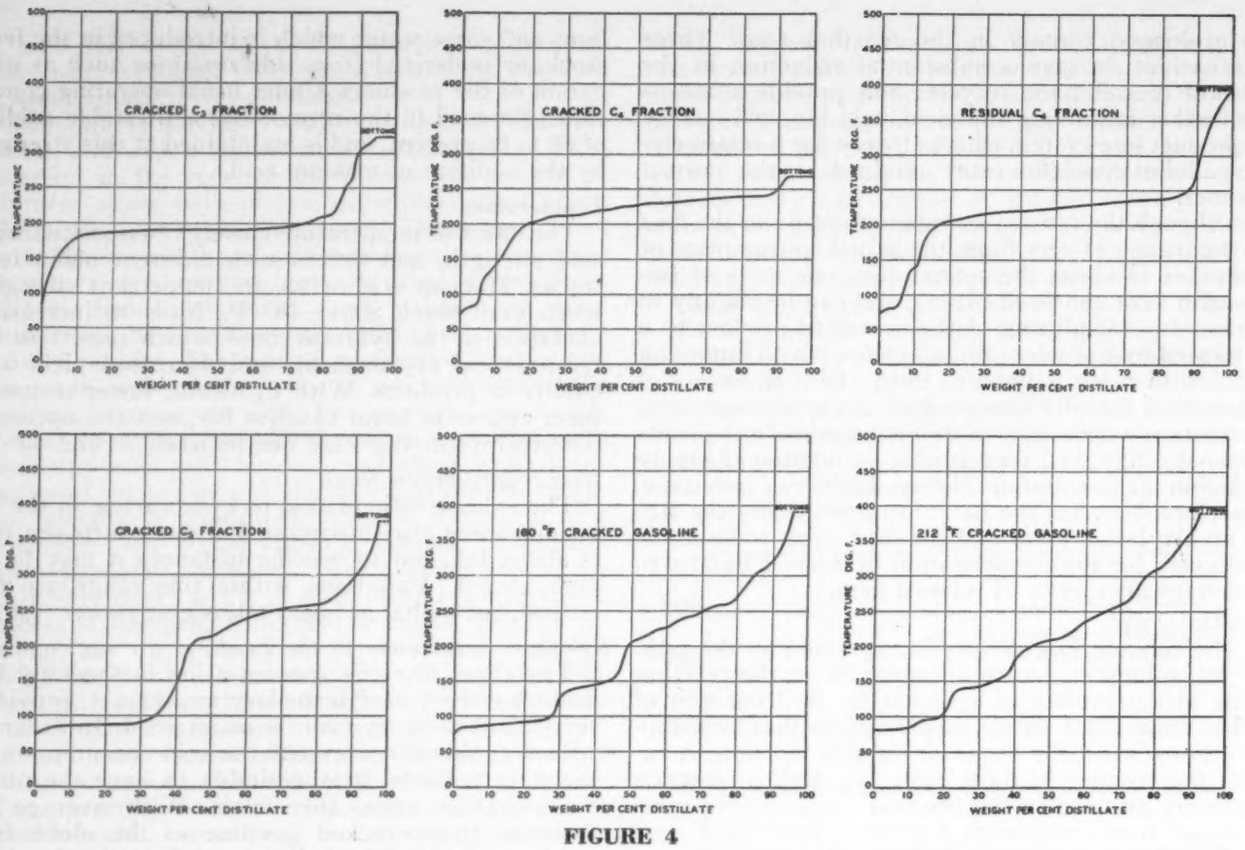

FIGURE 4

True-Boiling-Point Distillation of Total Alkylate from Isobutane and Representative Olefin Feed Stocks.

gasoline fractions containing C_5 hydrocarbons, or higher, in which the types of impurities and the composition and ratio of hydrocarbons are more likely to vary with the crude and the method of refining. In Table 1 a few representative feed stocks have been selected, and the operating conditions and yields to be expected are given. Representative precision distillation curves of the resulting products are shown in Figure 4. It will be seen that for the C_4 olefins the yields obtained are very close to theoretical. For the higher olefins from cracked-naphtha fractions, the yields are apparently less; this is due largely to the absorption of aromatics, dienes, or other similar components in the acid phase; and if these losses are deducted, excellent yields are obtained also on the higher olefins; and the products are fully saturated. The products formed are not entirely those expected from the straight coupling of the *iso*paraffin with the olefin. This is shown in the case of the alkylation of C_4 fractions, in which small *iso*pentane and hexane plateaus are found in the distillation curve of the products (Figure 4)—indicating the presence of C_5 and C_6 hydrocarbons in greater amount than could have been introduced with the feed.

The operating conditions given in Table 1 are typical for these feed stocks. However, they do not

TABLE 1

Alkylation with Representative Refinery Olefin Feed Stocks

Olefin Feed Stock (Percent by Weight of Olefin)	C_3 Fraction from Cracking 30[a]	C_4 Fraction from Cracking 48[b]	Residual C_4 Fraction from *Iso*octane Manufacture 24[c]	C_5 Fraction from Cracking 55	70° to 160° F. End-Point Cracked Gasoline 52	70° to 210° F. End-Point Cracked Gasoline 50
Conditions:						
*Iso*paraffin used	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane
Mole ratio of *iso*paraffin to olefin	8	5	5	8	8	8
Makeup acid strength, percent by weight of sulfuric acid	98–100	98–100	98–100	98–100	98–100	98–100
Volume ratio of acid to hydrocarbon ratio	1	1	1	1	1	1
Temperature, °F	85	32–50	32–50	50	50	50
Contact time, min.	20–40	20–40	20–40	20–40	20–40	20–40
Titratable acidity of rejected acid, as percent by weight of sulfuric acid	88–90	88–90	88–90	88–90	88–90	88–90
Percent by weight of yield of total alkylate based on olefin in feed	185	190–200	200–215	134[d]	126[d]	115[d]
Percent by volume of total alkylate based on olefin in feed	138	158–166	168–180	125[d]	119[d]	113[d]
Aviation fraction (end point, 300°F.) in total alkylate, percent	92–95	88–90	89–91	90	85	77
Makeup acid, lb. per gal. of total alkylate	2.6	1	<1	1.5	1.7	3.3

[a] With mixed C_3 and C_4 fractions, materially better results are obtained.
[b] About 18 percent *iso*butylene present.
[c] Largely butylene-2.
[d] Yield based on total refinery fraction, which includes saturates.

TABLE 2

Properties of Products from Alkylation with Representative Refinery Olefin Feed Stocks

Olefin Feed Stock	C_3 Fraction from Cracking	C_4 Fraction from Cracking	Residual C_4 Fraction from *Iso*octane Manfuacture	C_5 Fraction from Cracking	70° to 160° F. End-Point Cracked Gasoline	70° to 210° F. End-Point Cracked Gasoline
*Iso*paraffin Used	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane
Properties of total alkylate (C_4-free):						
Gravity, deg. API	72.1	69.2	69.2	76.6	72.1	70.6
Bromine No., g. of bromine per 100 ml.	0.1–0.4	0.3–0.5	0.3–0.5	0.5–0.1	0.5–0.1	1–2
Sulfur, per cent	0.001	<0.001	<0.001	<0.005	<0.005	<0.005
Reid vapor pressure, lb. per sq. in.	4	....	3	8	....	....
Octane No. (ASTM-CFR)	88.0	91.5	92.5	87.0	83.0	79.0
ASTM Distillation, in °F.						
Initial boiling point	152	120	117	108	126	128
End point	387	403	378	446	455	414
10-percent point	180	182	183	144	158	162
20-percent point	185	199	203	164	169	176
30-percent point	189	209	213	191	183	190
40-percent point	192	217	221	222	201	208
50-percent point	194	222	225	242	220	220
60-percent point	198	230	228	253	236	236
70-percent point	202	235	231	261	250	248
80-percent point	212	242	236	277	270	266
90-percent point	271	267	250	306	316	328
95-percent point	345	340	314	368	374	385
Recovery, percent	98	99	98.5	99	98	98
Recovery at 266 °F., percent	88	89.5	92	79	76	70
Properties of 300 °F. end-point fraction:						
Unsaturation, percent	Negligible	Negligible	Negligible	Negligible	Negligible	Negligible
Sulfur, percent	Negligible	Negligible	Negligible	Negligible	Negligible	Negligible
50-percent point, °F	190	220	221	209	200	205
Reid vapor pressure, lb. per sq. in.	....	3.5	3.0	9.0	11.6	7.4
Octane No. (ASTM-CFR)	89	92	93	87	82	78

[a] Products not depentanized.

represent necessarily the best results which have been obtained. It will be noted that higher *iso*butane-olefin ratios are used with propylene and the higher olefins than are used with C_4 olefins. This is done to reduce the acid consumption. The contact times are similar, and the strength of the rejected acid is the same. The acid consumption varies with the feed used, and is the highest in the case of gasoline with an end point of 210° F. Cracked C_3 fraction, free of butylene, also shows a high acid consumption.

The ASTM distillation and other data pertinent to the evaluation of these products for aviation fuels are given in Table 2. It will be seen that both the total product of the reaction and the aviation fraction derived from it are substantially sulfur-free and saturated. Even when cracked gasolines of high

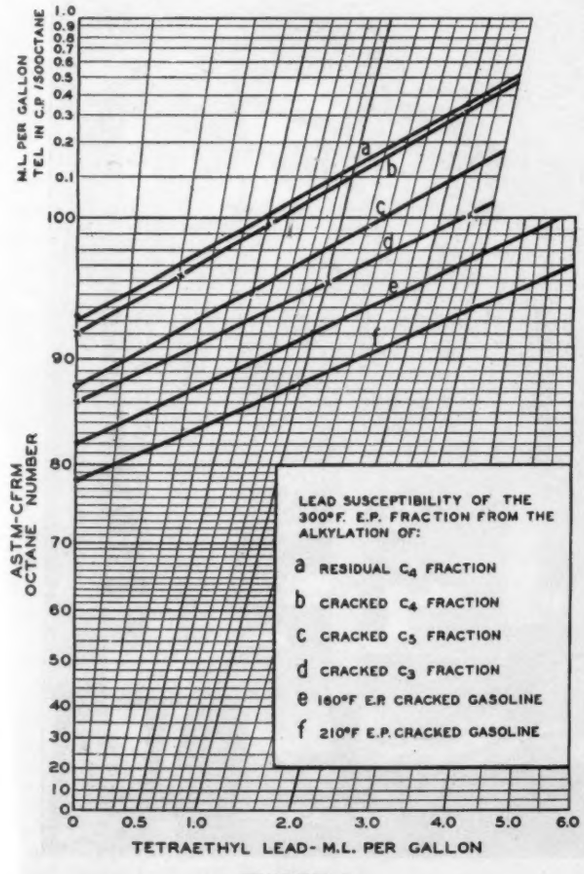
M.L. PER GALLON TEL IN C.P. ISOOCTANE
ASTM-CFRM OCTANE NUMBER
TETRAETHYL LEAD - M.L. PER GALLON
LEAD SUSCEPTIBILITY OF THE 300°F. E.P. FRACTION FROM THE ALKYLATION OF:
a RESIDUAL C4 FRACTION
b CRACKED C4 FRACTION
c CRACKED C5 FRACTION
d CRACKED C3 FRACTION
e 160°F E.P. CRACKED GASOLINE
f 210°F E.P. CRACKED GASOLINE

FIGURE 5

Lead Susceptibility of the 300°F.-End-Point Fraction from Alkylation.

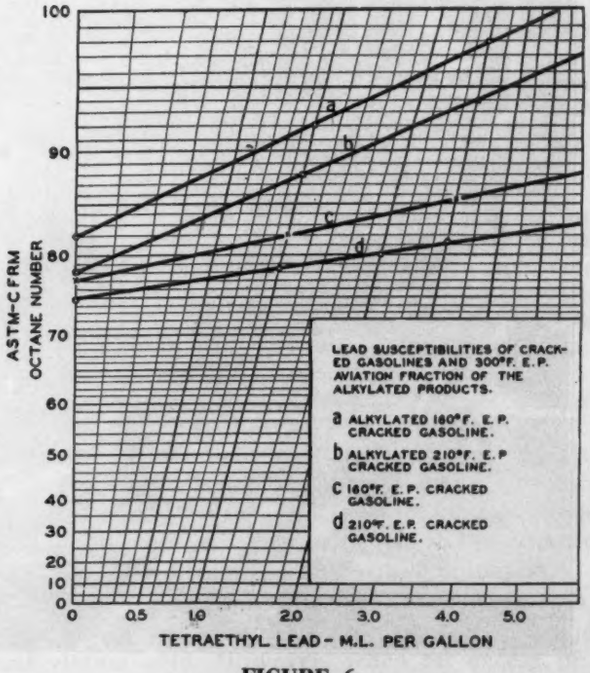
ASTM-C FRM OCTANE NUMBER
TETRAETHYL LEAD - M.L. PER GALLON
LEAD SUSCEPTIBILITIES OF CRACKED GASOLINES AND 300°F. E.P. AVIATION FRACTION OF THE ALKYLATED PRODUCTS.
a ALKYLATED 160°F. E.P. CRACKED GASOLINE.
b ALKYLATED 210°F. E.P. CRACKED GASOLINE.
c 160°F. E.P. CRACKED GASOLINE.
d 210°F. E.P. CRACKED GASOLINE.

FIGURE 6

Lead Susceptibility of Cracked Gasolines and 300° F.-End-Point Aviation Fraction of the Alkylated Products.

sulfur content are used as feed stocks, the product is sulfur-free, but the catalyst consumption is increased by the presence of the sulfur. Samples of alkylation products have been exposed to strong sunlight for months without recognizable discoloration or gum formation.

Data showing the clear ASTM-CFR octane number and the lead susceptibility of the various products are given in Figure 5. For comparison, the lead susceptibility of an untreated gasoline with an end point of 160°F. and one with an end point of 210°F. is shown in Figure 6. It will be seen that these gasoline fractions after alkylation have such a greatly-improved lead susceptibility that it is possible to produce 95-octane gasoline with moderate amounts of lead.

All of the alkylation products given in Table 2 are excellent blending stocks for 100-octane aviation fuels. It is not within the scope of this paper to discuss the wide number of possible blends. Their

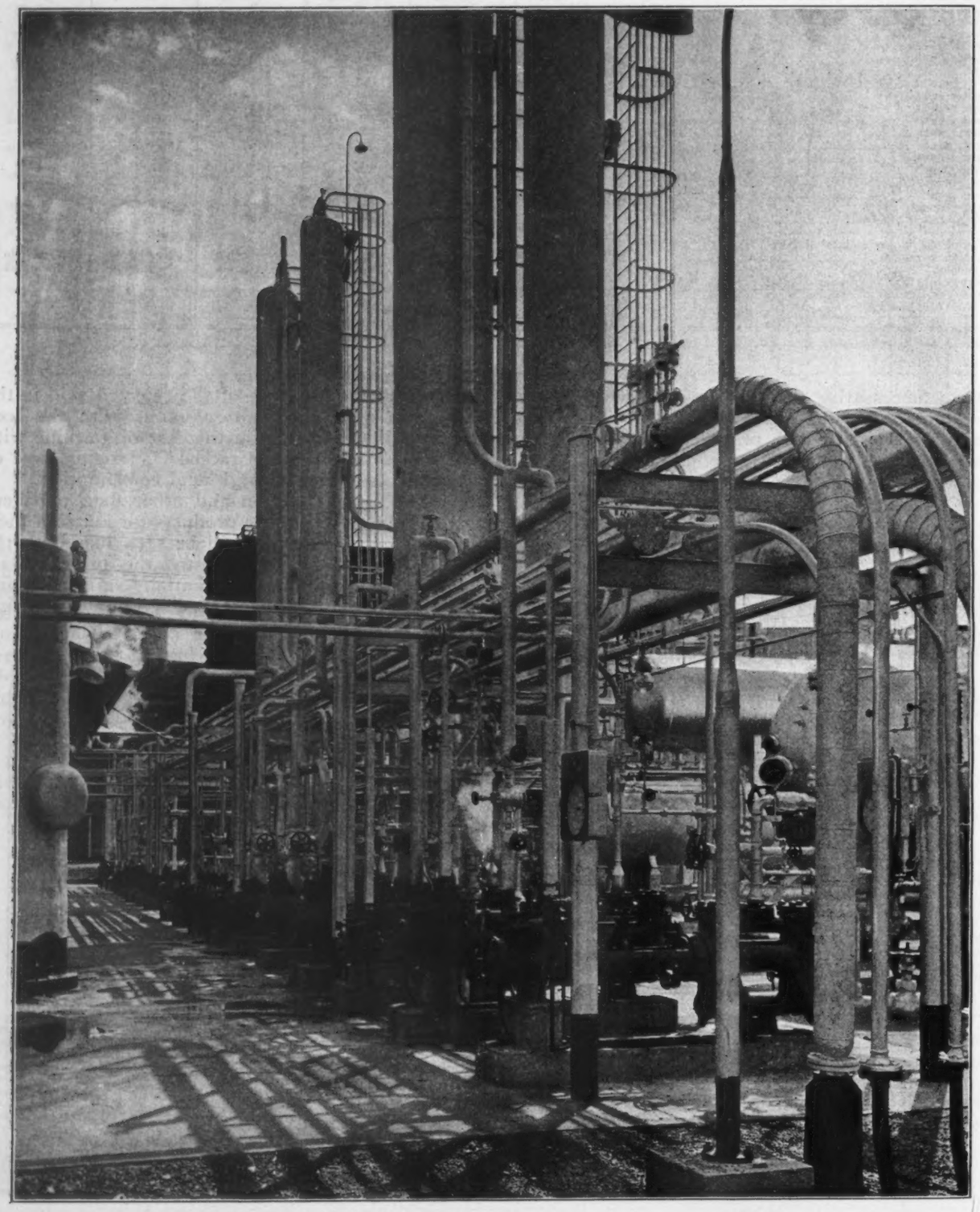

FIGURE 7

Martinez Alkylation Plant of Shell Oil Company.

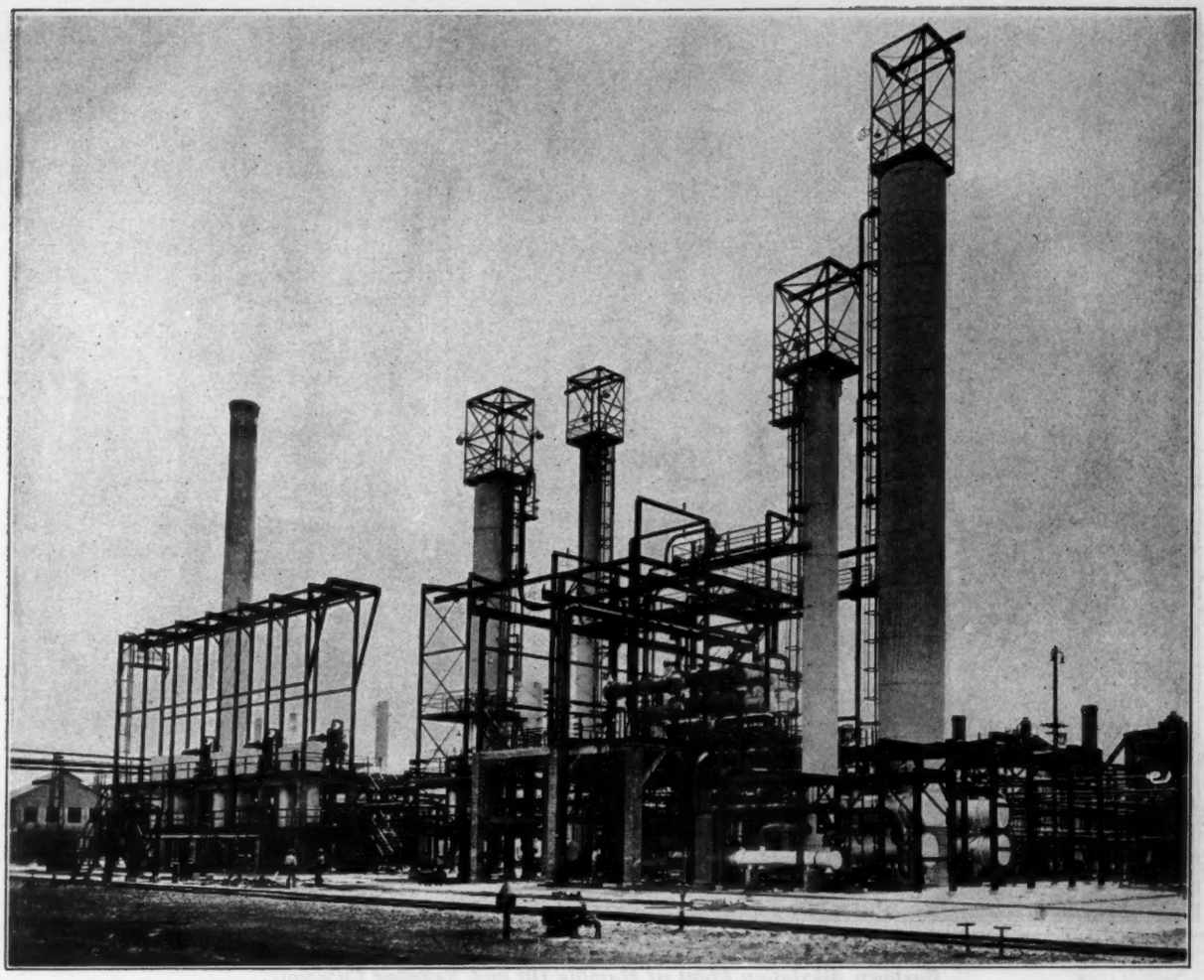

FIGURE 8
Port Arthur Alkylation Plant of The Texas Company.

composition may vary widely, depending on the base stock used and the alkylate chosen; but sufficient data already have been presented to allow those familiar with the art to prepare blends suitable to their own refinery conditions. For illustrative purposes, one such blend prepared from 50 percent of C_4 aviation alkylate and 50 percent of 77-octane straight-run gasoline base stock is given in Table 3. Similar blends may vary over the range of 40 to 70 percent of aviation alkylate, depending on the properties of the stocks.

A large percentage of the alkylation products can be prepared to meet the volatility requirements of aviation fuels, without blending. Therefore, when there is a demand for fuels having anti-knock properties superior to unleaded *iso*octane, these super fuels can be made from selected alkylation fractions by leading.

The alkylation products boiling above the normal aviation range also have high octane values and good lead susceptibilities, and thus ideally are suited for use when, in addition to these desirable properties, low volatility is required.

TABLE 3
Characteristics of 100-Octane Aviation Gasoline

Gravity, deg. A.P.I.	71.8
Octane No., clear (ASTM-CFR)	85
Octane No. plus 3 ml. tetraethyl lead (Army)	100
Copper-dish gum, mg. per 100 ml.	1
Acid heat, deg. F.	2
Freezing point, deg. F.	Below —76
Reid vapor pressure, lb. per sq. in.	7
50-per-cent point, deg. F.	207
End point, deg. F.	308

ACID REQUIREMENTS

It will be seen in Table 1 that the acid consumption differs for various feed stocks, and is least for the case in which *iso*butane is alkylated with C_4 olefins. However, as has been pointed out already, the acid is not consumed in the chemical sense, but merely has been diluted by absorbed hydrocarbons and water. It usually is withdrawn from the reactor at a titratable acidity of about 88 to 90 percent, and in this form it can be used elsewhere in the refinery for acid treating naphthas or light fuel oils. It has been found that, on the basis of the sulfuric-acid content, the rejected acid from alkylation is equivalent to fresh acid for gum reduction, but is not quite as efficient as fresh acid for sulfur reduction.

In many cases the acid-treating requirements of a refinery are sufficient to utilize all of the rejected alkylation acid. However, when an excess of acid exists, it is possible to recover and reconcentrate it for further use in alkylation. This usually is done

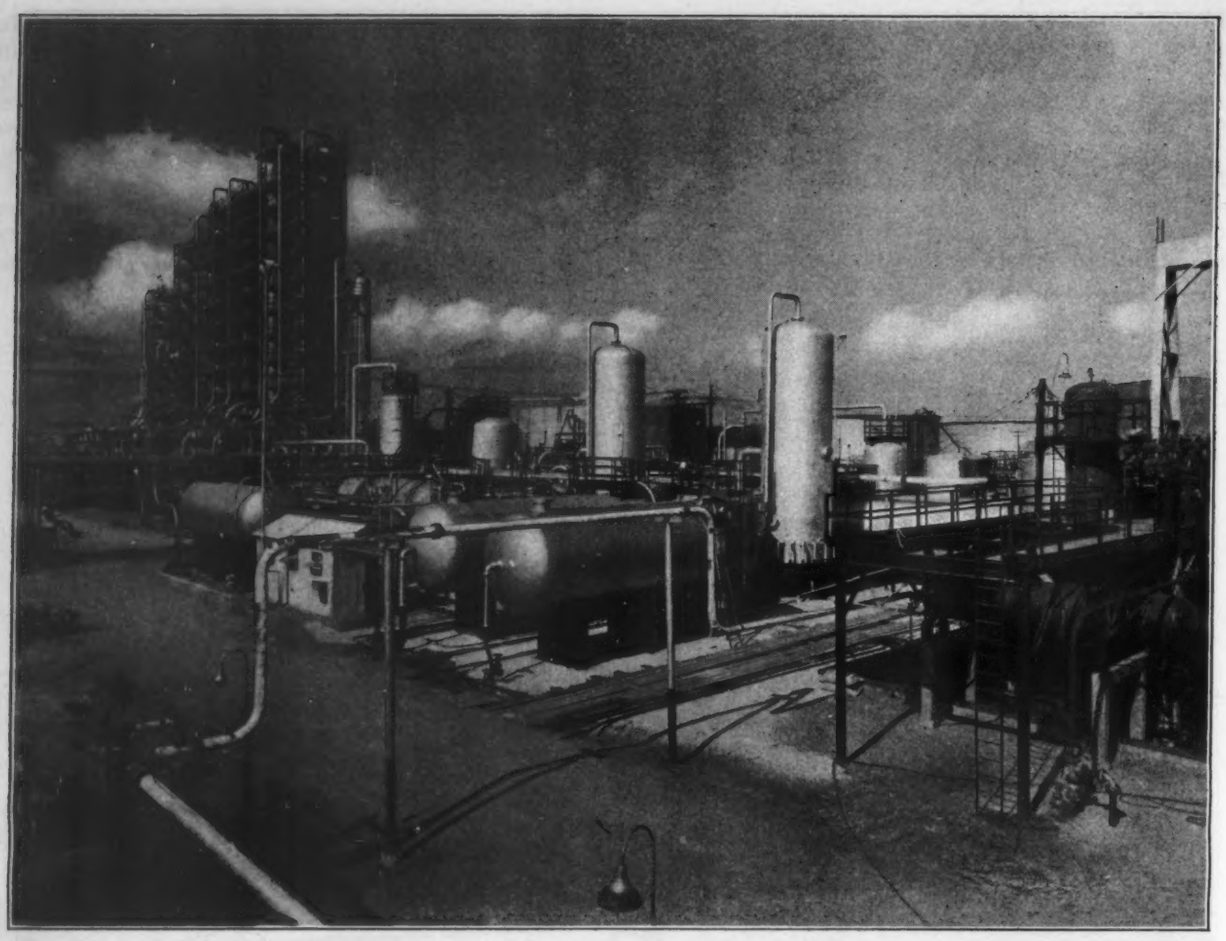

FIGURE 9
Baytown Alkylation Plant of Humble Oil and Refining Company.

first by diluting the acid to about 50 percent to release the dissolved oil. This amounts to about 6 to 8 percent of the used acid and, on dilution, it separates as an upper layer which can be drawn off. The acid is then substantially free of organic material, and conventional methods can be used for reconcentration. Thus the actual cost of the catalyst can be reduced to an extremely low figure.

TABLE 4

Comparison of Alkylation and Polymerization for C_4 Fraction from Cracking

Feed composition, percent by volume:				
Propane	1			
*Iso*butylene	18			
*n*Butylenes	30			
*Iso*butane	9[e]			
*n*Butane	42			
Total	100			
Method Used	**Cold-Acid Absorption and Polymerization Plus Hydrogenation**	**Catalytic Polymerization Plus Hydrogenation[a]**	**Catalytic High Pressure Polymerization Plus Hydrogenation[b]**	**Alkylation**
Addition *iso*butane, gallons per gallon of feed	Nil	Nil	Nil	0.42
Product[c] boiling below 300 °F., gallons	0.11	0.25	0.32	0.73
Octane No. of saturated aviation cut (ASTM-CFR)	99–100	96–98	91–93	92–94
Gallons of 87-octane fuel per gallon of feed prepared by blending aviation cut with 72-octane base stock[d]	0.21	0.42	0.43	1.02

[a] Either UOP or hot-acid process operating for maximum octane number.
[b] Operating for maximum yield.
[c] Data are approximate. The yield depends somewhat on operating conditions.
[d] Assuming straight-line function and motor-method octane numbers.
[e] In general, refinery streams are richer in *iso*butane.

COMMERCIAL ASPECTS

One of the basic factors to be considered in the installation of a commercial alkylation plant is the availability of the *iso*paraffin, and in most cases this is the factor limiting the capacity of a given plant. With a given supply of *iso*paraffin, an approximately equal amount of olefin can be converted by alkylation; and on this basis alkylation offers a very distinct advantage, from a yield and process standpoint, over the two-stage process of polymerization and hydrogenation. In Table 4 a comparison is given for the different processes when using a C_4 fraction from cracking. It will be seen that the yield of the 87-octane unleaded aviation gasoline is markedly greater by alkylation. The table also illustrates the great advance made in the manufacture of aviation fuels by the petroleum industry during the past five years.

With other olefin feed stocks, alkylation is even more advantageous. Whereas the alkylate from propylene has an octane number of 88, catalytic polymerization of propylene leads to a polymer of relatively low octane number which, on hydrogenation, is degraded further. Catalytic polymerization of C_5 or higher olefins is not commercial.

The sulfuric-acid alkylation process is basically a new development. However, the equipment employed is of standard type, and its practicability is demon-

strated amply by the fact that similar equipment has been used for the manufacture of *iso*octanes by the hot-acid and cold-acid processes for nearly five years without any major replacements being necessary. Also, as the sulfuric acid used as the alkylation catalyst is of high concentration and the plants are operated at below atmospheric temperature, corrosion is negligible—and steel equipment can be used throughout. The auxiliary fractionating equipment is of standard type, and presents no difficulties in design and construction. Thus no new nor very troublesome engineering principles are encountered, and competent engineering service is available for construction of plants. Individual requirements vary widely, and require study to determine the particular conditions to be used in each case.

Alkylation is a commercially-proven process. The development has been extremely rapid, due to cooperative effort; and at present there are six commercial plants in operation, and a number of plants under construction. A list of these plants, together with their rated capacities, is given in Table 5. Photographs of several of the plants now in operation are given in Figures 7, 8 and 9. The results from the commercial plants are fully up to expectation.

CONCLUSION

As the result of the combined efforts of the research staffs of five major oil companies, the alkylation process has been developed to proven commercial success; and it has been found to be suited ideally to the manufacture of high-octane fuels. Several commercial plants are being operated or are in the process of construction, and a new method of gasoline manufacture has been achieved which undoubtedly will affect the petroleum industry as a whole, and contribute greatly to aviation progress.

TABLE 5

Alkylation Plants in Operation and under Construction

Company	Location	Aviation Alkylate (Barrels Per Day)
OPERATING		
Humble Oil and Refining Co.	Baytown, Tex.	1,200
Shell Oil Co.	Dominguez, Calif.	800
The Texas Co.	Port Arthur, Tex.	750
Shell Oil Co.	Martinez, Calif.	500
Standard Oil Co. of New Jersey	Bayway, N. J.	175
Anglo-Iranian Oil Co.	Abadan, Iran	100
UNDER CONSTRUCTION OR CONSIDERATION		
Humble Oil and Refining Co.	Baytown, Tex.	1,500
Lago Oil and Transport Co.	Aruba, Netherland West Indies	520
Magnolia Petroleum Co.	Beaumont, Tex.	2,140
N. K. P. M.	Palembang, Sumatra	560
Shell Oil Co.	Houston, Tex.	1,500
Shell Oil Co.	Wood River, Ill.	1,500
Standard Oil Co. of Louisiana	Baton, Rouge La.	1,200
Union Oil Co. of California	Wilmington, Calif.	270

BIBLIOGRAPHY

[1] Heron and Beatty, *J. Aeronautical Sciences* **5** [12] (1938).

[2] Ziegenhain, *Oil Gas J.* **37** [25] 11 (1938).

[3] McAllister, "The Catalytic Polymerization of Butylenes by Sulfuric Acid," *Proc. API* **18** [III] 78 (1937); also *Oil Gas J.* **36** [26] 139 (1937). Egloff, Morrell, and Nelson, "Motor Fuels from Polymerization," *Proc. API* **18** [III] 64 (1937); also *Oil Gas J.* **36** [26] 176 (1937).

[4] Birch, Dunstan, Fidler, Pim, and Tait, *Am. Chem. Soc.* meeting, Baltimore, Apr. 3-7 (1939).

[5] Birch, Dunstan, Fidler, Pim, and Tait, *J. Inst. Petroleum Tech*, **24**, 303-20 (1938).

Thermal Alkylation

[*Continued from page 115*]

Considering Table 8 and Figure 3, blending ingredients were selected possessing the characteristics thought to be most representative of high octane number blending ingredients. Of the four ingredients, the neohexane and isopentane are least subject to variation in their characteristics. The isooctane may range in octane number from 90 to 98. The effect of the octane number variation can be calculated as was done in the example given. In general, the effect will be to raise or lower the entire octane number level as represented in Figure 3 with very little effect on the differences in octane number. The blending naphthas are subject to octane number variation and to a considerable range in volatility. However, since maximum neohexane will be of most usefulness in attaining the maximum octane numbers and since such blends will contain very little or no naphtha, the characteristics of the naphtha are of relatively little importance.

For every set of corresponding blending ingredients, a diagram similar to Figure 3 can be prepared and in each case there will be a pronounced increase in the maximum octane number attainable for a given midpoint volatility when neohexane is used.

BIBLIOGRAPHY

[1] T. S. Sligh, Jr., "Progress in the Measurement of Motor Fuel Volatility," *S.A.E. Journal*, **18**, 393 (1926).

[2] O. C. Bridgeman, "Present Status of Equilibrium-Volatility Work at Bureau of Standards," *S.A.E. Journal*, **25**, 345 (1929).

[6] G. G. Brown, "The Volatility of Motor Fuels," Engineering Research Bulletin No. 14, Univ. of Michigan (1930).

[4] V. N. Ipatieff and A. V. Grosse, "Reactions of Paraffins with Olefins," *J. Am. Chem. Soc.*, **57**, 1616 (1935).

[5] V. N. Ipatieff and A. V. Grosse, "Action of Aluminum Chloride on Paraffins," *Ind. Eng. Chem.*, **28**, 461 (1936).

[6] V. N. Ipatieff, A. V. Grosse, Herman Pines and V. I. Komarewsky, "Alkylation of Paraffins with Olefins in the Presence of Aluminum Chloride," *J. Am. Chem. Soc.*, **58**, 913 (1936).

[7] F. E. Frey and H. J. Hepp, "Noncatalytic Addition of Ethylene to Paraffin Hydrocarbons," *Ind. Eng. Chem.*, **28**, 1439 (1936).

[8] V. N. Ipatieff, *Catalytic Reactions at High Pressures and Temperatures*, Macmillan Company, New York (1936).

[9] F. E. Frey and H. J. Hepp, "Motor Fuel Isoparaffins by Thermal Gas Polymerization," *Oil and Gas J.*, **35**, No. 34, 40 (1937).

[10] H. M. Trimble and J. O. Richardson, "Tetraethyl Lead Responsiveness of Two Hydrocarbons," *Oil and Gas J.*, **36**, No. 46, 130 (1938).

[11] S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait, "Saturated High Octane Fuels without Hydrogenation. The Addition of Olefins to Isoparaffins in the Presence of Sulfuric Acid," *J. Inst. Petroleum Tech.*, **24**, 303 (1938).

[12] S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait, "Condensation of Olefins with Isoparaffins in Sulfuric Acid," *Oil and Gas J.*, **37**, No. 6, 49 (1938).

[13] S. F. Birch and A. E. Dunstan, "Some Problems Associated with Olefin-Isoparaffin Addition Reactions," *Trans. Faraday Soc.*, **35**, 1013 (1939).

[14] F. H. Blunck and D. H. Carmody, "The Catalytic Alkylation of Isobutane with Gaseous Olefins," paper before Am. Chem. Soc. meeting, Baltimore, Md., April, 1939.

[15] V. N. Ipatieff, "Catalytic Refining Trends," *Oil and Gas. J.*, **37**, No. 46, 86 (1939).

[16] S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait, "High-Octane Isoparaffinic Fuels. Production by the Addition of Olefins to Isoparaffins," *Ind. Eng. Chem.*, **31**, 884 (1939).

[17] S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait, "High-Octane Isoparaffinic Fuels. Production by the Addition of Olefins to Isoparaffins," *Ind Eng. Chem.*, **31**, 1079 (1939).

[18] Mildred M. Hicks-Bruun, Johannes H. Bruun and W. B. Mason Faulconer, "Isolation of the Missing Isomer of Hexane (2,2-Dimethylbutane) from Natural Gas and Determination of Its Physical Properties," paper before Am. Chem. Soc. meeting, Boston, Mass., Sept., 1939.

Catalytic Reforming *for the Production of* Aviation Gasoline

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THE paper describes the application of the Houdry catalytic process to the reforming of gasolines and naphthas into aviation-base gasoline. Brief descriptions are included showing results obtained when motor fuel is the product of the reforming operation. Yields and product characteristics are given. Advantages claimed for the process consist of high yields of high-octane chemically-stable base gasoline with high susceptibility to addition agents and blending materials; flexibility of operation; high liquid recoveries; and equipment proven by large-scale commercial installations as satisfactory from an operating standpoint.

This paper was presented at Twentieth Annual Meeting, American Petroleum Institute, Chicago, November 17, 1939.

THE purpose of this paper is to present a description of the application of the Houdry catalytic process to the reforming of gasoline and naphtha into aviation-base gasoline, together with results obtained and a discussion of the flexibility and benefits to be obtained from the operation.

A—General Description

The process, catalyst, and apparatus used in the operations described hereinafter constitute subject matter from more than 100 U. S. patents, and are included in numerous corresponding foreign patents and pending U. S. and foreign applications.

The importance of a source of supply of high-octane aviation gasoline has been emphasized greatly by recent world events. There are available today many processes for the production of blending agents or blending materials. Such materials are not usually complete aviation fuels, but are added to base materials to improve or impart to such bases desirable and necessary characteristics, such as ability to give proper combustion characteristics in high-compression aviation motors. Among such blending materials are tetraethyl lead, and hydrocarbons such as *iso*octane, *iso*pentanes, or alkylates. These materials are added to a base gasoline of proper boiling point and chemical stability to produce the finished material. Among the important requirements of a desirable aviation fuel are: sufficient stability to resist or prevent the formation of objectionable gum or oxidation products in storage and in use; sufficiently low sulfur content to prevent corrosion; proper hydrocarbon composition to give the necessary combustion characteristics; and the required vapor pressure to prevent vapor lock. The aviation base must be derived from a source of supply of the necessary magnitude to permit immediate availability of large quantities from existing equipment.

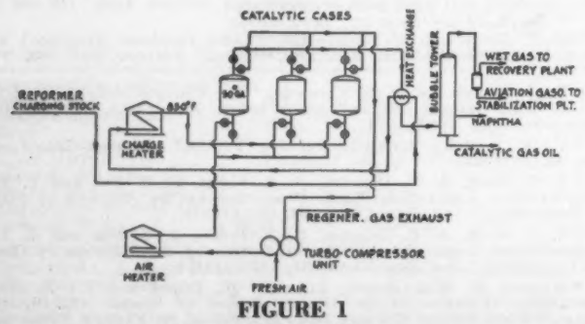

FIGURE 1
General Flow Diagram

Inasmuch as the availability of blending agents necessarily is limited to the raw materials and plant facilities available, the base gasoline should have the characteristics of being highly susceptible to the addition of blending agents, i. e., should require a minimum quantity of such agents to reach the necessary standards.

The supply of straight-run gasoline and naphtha is, within the requirements of the field of aviation fuels, unlimited. However, in view of existing plant facilities for the production of such blending materials as *iso*octane, only certain straight-run gasolines have sufficiently high octane rating to be suitable for aviation-base stock. Even though the number of units capable of supplying *iso*octane and alkylates was increased greatly, the cost of producing such materials to improve straight-run aviation fuels to the necessary extent must be examined carefully.

As a solution in part to this problem, the Houdry catalytic-reforming operation has been developed. Units for this method of producing aviation-base fuels are being erected in France and the United States, the combined charging capacity of which amounts to approximately 25,000 barrels per day.

B—Description of Catalytic-Reforming Unit

The flow sheet (Figure 1) shows the type of unit used. The charge, either a gasoline with a final boiling point of from 400 to 500° F., or a naphtha boiling between 250 and 500 °F., is pumped through heat ex-

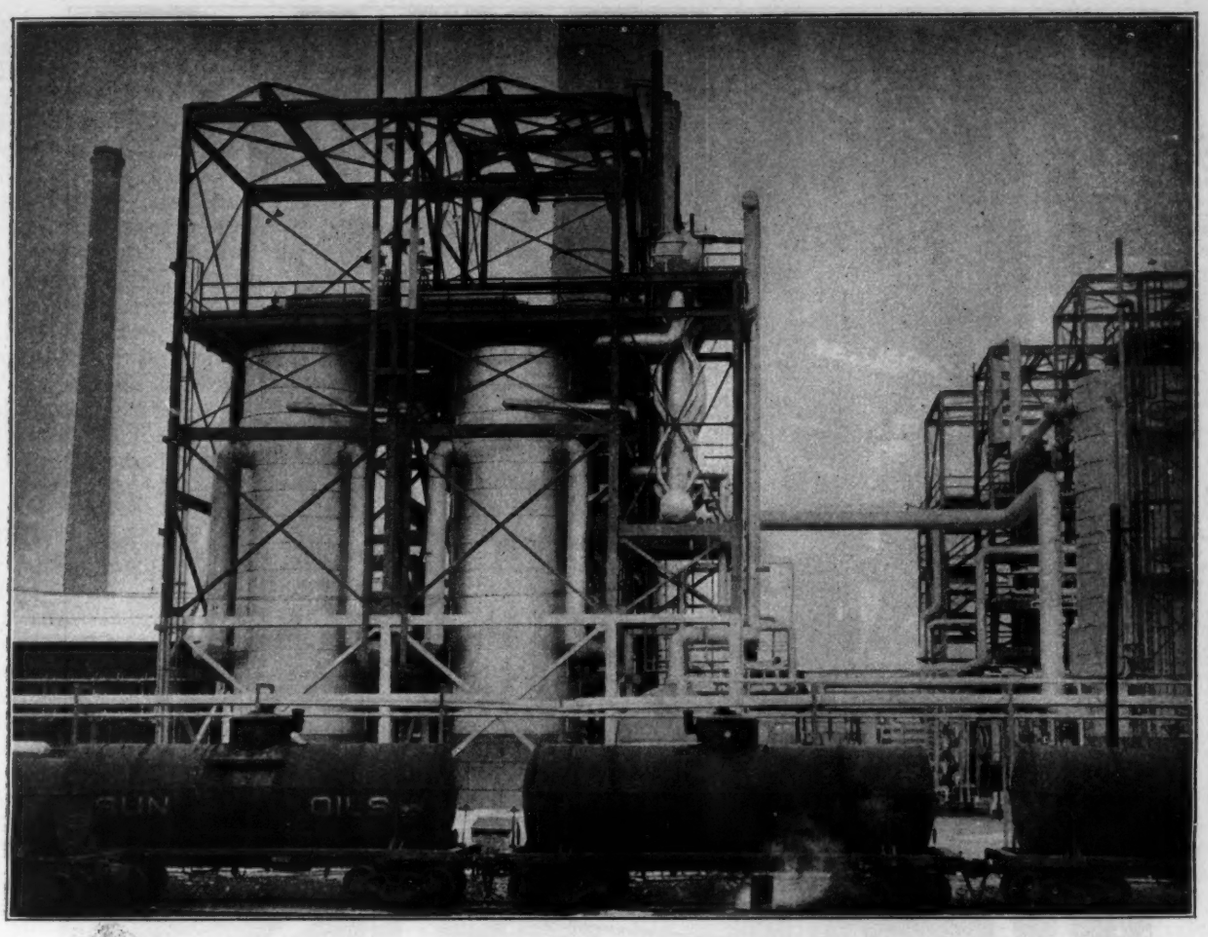

FIGURE 2
Houdry Unit for Reforming Naphtha or Treating Gasoline

changers to a still, wherein it is vaporized and heated to 850 °F. The vapors pass directly to the catalyst chambers; thence, after passing through the catalyst flow, through heat exchangers to a fractionating tower, and are separated into aviation gasoline, naphtha, gas oil, and gas. As a result of the reactions on the catalyst, a carbonaceous deposit is formed which is oxidized periodically or burned by controlled amounts of air—thus regenerating the catalyst for further use. The products of regeneration are passed directly to a gas turbine, and expanded to atmospheric pressure—thus creating the necessary energy to enable the turbine to operate an axial turbocompressor which supplies the air for regeneration. The air is heated to proper temperature, and admitted to the catalyst cases for regeneration.

The catalyst cases are on oil stream for 10 minutes, and are regenerated over a period of 20 minutes. Three cases thus are required—one on stream, two on regeneration, permitting a continuous flow of vapors to the catalyst. All equipment is a duplicate in type of that used in operating Houdry units processing gas oils and residual fuels for motor gasoline. Such equipment now is processing 180,000 barrels per day, and in certain instances has been in successful operation for several years. This is mentioned to indicate the proven mechanical perfection and operability of this type of reforming operation.

A Houdry catalytic-reforming plant, without change, may be used to produce motor gasoline from naphtha, or may charge gas oil at decreased throughput to produce either aviation or motor gasoline. For example, when charging East Texas or Coastal naphthas, the throughput rate is two volumes of oil (measured as liquid) per hour per one volume of catalyst; whereas when charging gas oils the rate is one volume of oil per volume of catalyst. The catalyst employed in this operation is a highly-active hydrosilicate of alumina. Such a catalyst costs approximately $25,000 for a plant charging 10,000 barrels of naphtha per day, and its life is such that replacement is required at intervals of not less than 180 stream-days.

The cost of installing an 8,500-barrel per-day unit is approximately $1,225,000 within the battery limits, excludi g royalty. A 10,000-barrel unit is being installed on an existing pipe still at a cost of $862,000—the heater, fractionating equipment, and control house of the old unit being utilized.

The direct cost of operation is normal to thermal reforming. The fuel requirement is less than for thermal reforming. Net power consumption is about the same, as the power for the air compressor is supplied by the regeneration operation. Number of operators per shift is the same as for a similar thermal operation. Maintenance is estimated at 3 percent of the capital investment per year.

Depreciation is in excess of a thermal reformer to the extent that the capital cost of the catalytic equipment exceeds that of a thermal unit. Considering the quality of the products obtained, the cost per unit of product is

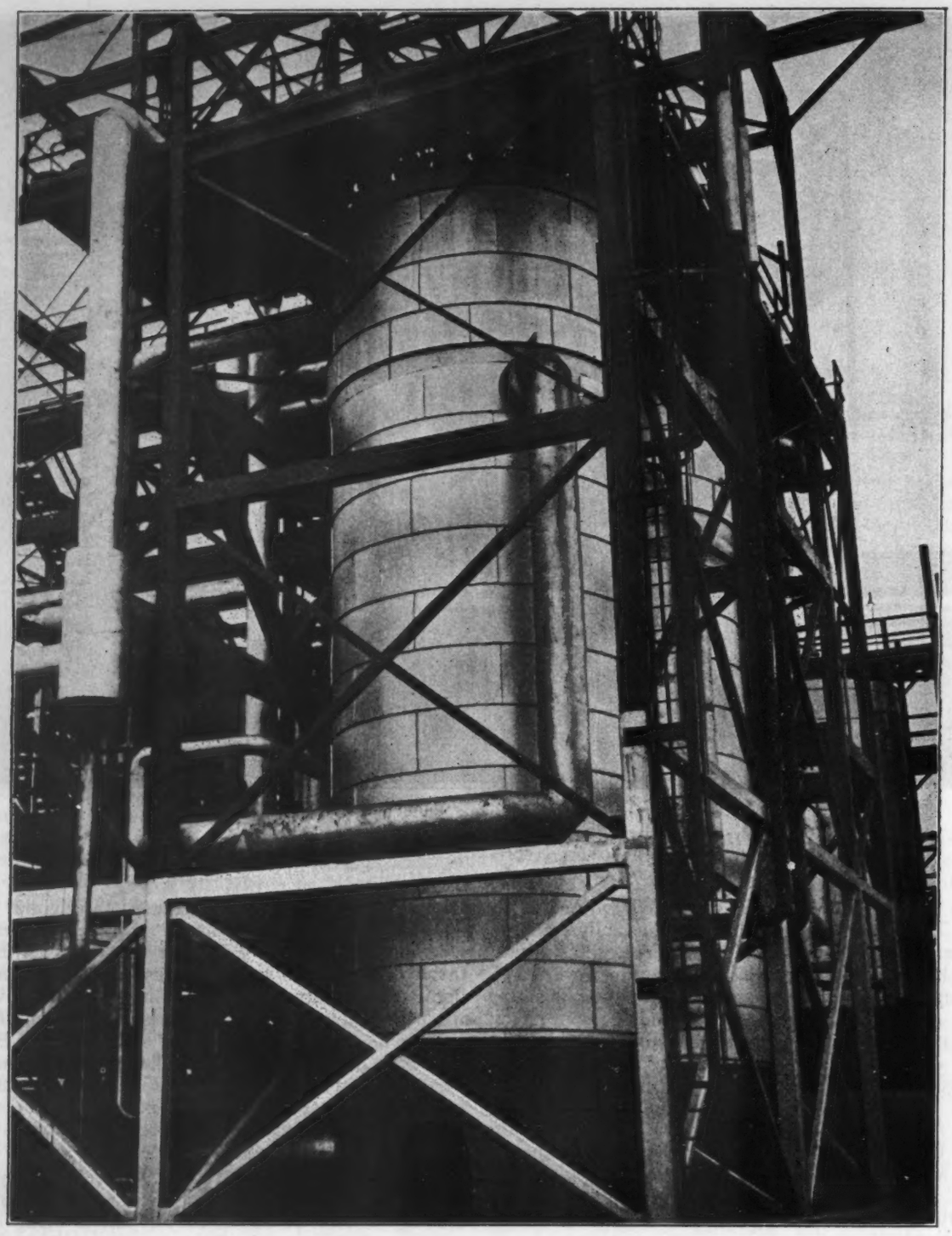

FIGURE 3
Close-up View of Houdry Converter

believed to be highly favorable as compared to thermal reforming.

YIELDS AND PRODUCT CHARACTERISTICS

The distillation range of the charging stock for reforming depends upon the type of crude. When charging stocks such as East Texas naphtha, the light ends are removed to give the naphtha an initial boiling point between 280 and 350 °F., and an end point of 400 to 500 °F. For naphthas from highly-naphthenic crudes, the range is from an initial of 90 °F. to a final of 500 °F. Table 1 shows the product yields from two such charging stocks.

Table 2 shows the characteristics of the charging stocks and products corresponding to the yields given in Table 1.

Table 3 shows the analysis of gas produced by the operation corresponding to Tables 1 and 2.

Discussion of Tables

The yields of aviation gasoline shown in Table 1 are based upon European aviation specifications, which call for 90 percent evaporated at 293 °F. To meet U. S.

specifications of 90 percent at 257 °F., these yields must be decreased correspondingly.

The East Texas catalytic heavy naphtha shown may be reformed thermally to yield 73 percent of 410° F.-end-point gasoline of 73 octane number (ASTM), 17 percent gas oil of 700 °F. end point, and the balance gas. It is somewhat more refractory than virgin stock; but gives, under proper conditions, the same rise in octane for the same liquid recovery as do virgin stocks from the same crude. The gas-oil product likewise may be thermally cracked, and has been found to be at least equivalent to fresh stock of the same boiling-point and gravity relationship. Attention is invited to the low percentage of unsaturates in the gas analysis shown in Table 3. Table 2 shows the high susceptibility to lead characteristic of this aviation-base gasoline. If in the case of the product from East Texas naphtha it is desired to reduce the acid heat, it may be brought to 15 °F. with 3 lb. of acid per barrel, with a 3-percent loss.

Table 4 shows the stability of Houdry aviation gasoline leaded to the octane number required by aviation motors when subjected to severe operating conditions in a supercharged motor. This gasoline has demonstrated its ability to retain its anti-knock quality substantially unchanged, under these conditions, as opposed to aromatic fuels, such as benzene, which lose octane value under the same conditions. Thermally-cracked fuels do not possess the stability of the catalytic gasoline described herein. The necessity of octane stability under severe conditions is of prime importance, especially in air-cooled aviation engines.

The aromatic compound, benzene, has dropped to as low as 95 octane at the most severe conditions, from an original value of 100+0.6 ml. tetraethyl lead; whereas the Houdry aviation and straight-run containing 3 to 6 ml. tetraethyl lead have increased 4 to 5 numbers.

That the catalytic gasoline does not rely on a high concentration of aromatics for its high octane is apparent from the following analyses, in Table 5, of aviation-gasoline samples derived from a paraffinic and naphthenic crude. Much of the good octane value is due to the high *iso*paraffin content of the gasolines.

Table 6 shows the susceptibility of Houdry aviation gasoline to blending with *iso*octane.

Table 7 shows results obtained when using a Houdry unit as a reformer for the production of motor fuel. It will be noted that the results are obtained at different rates through the catalyst, and that all the rates are high. In each instance lower rates would give higher octane rating, and lower yields of gasoline. In all cases a high yield of highly-stable gasoline of excellent color, low gum and sulfur, and high lead susceptibility is obtained. When charging West Texas naphtha at the high rate almost complete desulfurization (0.21 to 0.01 percent sulfur) occurs, with a loss of but 5 percent of liquid. This is accompanied by an increase in octane number and in lead susceptibility; so that the addition of 1.5 ml. of tetraethyl lead results in a fuel of 75 octane number.

Because of probable wide fluctuations in demand for aviation gasoline, the alternate use of a reforming unit to crack gas oils is important. Such an operation is shown in Table 8. The yields and properties of both aviation and motor fuels are outstanding. Although the acid heat of the aviation fuel is higher than that from naphtha, it can be reduced by light acid treating to below 20 °F. without lowering the octane number of the leaded gasoline. This alternate use does not involve a catalyst change.

In conclusion, the Houdry reforming operation offers

TABLE 1
Aviation-Gasoline Yields

Charge to Plant—Percent of Crude:	Straight-run Naphtha—Grade "B" Coastal Crude (Gravity, 29.7 Deg. API) 39.9 (Initial)	Heavy Naphtha—East Texas Crude 19 to 39
Aviation gasoline, percent by volume	58.8	32.5
Motor naphtha, percent by volume	18.8	53.0
Cracked gas oil, percent by volume	9.1	
Dry gas, percent by weight	13.1	13.7
Catalyst deposit, percent by weight	2.3	2.4

TABLE 2
Inspection of Charge and Products*

	Grade "B" Coastal Naphtha				East Texas Naphtha		
	Charge	Aviation Gasoline	Motor Naphtha	Catalytic Gas Oil	Charge	Aviation Gasoline	Catalytic Heavy Naphtha
Gravity deg. API	46.8	60.1	39.5	25.2	46.2	64.0	41.7
ASTM Distillation, in °F.:							
Initial boiling point	154	104	311	412	282	104	314
5 percent point	206	130	317	424	302	120	331
10 percent point	224	144	322	430	324	132	336
20 percent point	252	166	327	436	334	144	344
30 percent point	278	184	331	440	344	157	351
40 percent point	305	199	336	446	356	174	358
50 percent point	334	212	340	454	366	198	368
60 percent point	362	226	346	464	376	220	379
70 percent point	388	242	353	476	388	242	391
80 percent point	410	256	361	498	403	262	412
90 percent point	435	276	380	544	424	288	445
95 percent point	448	300	391	620	440	298	476
End Point	464	328	416	694	454	334	597
Recovery, percent	98	98	98	98	98	97	98
Residue, percent	1.0	0.8	0.6	1.6	0.8	0.9	...
Color, Saybolt	18	30	...	...	30	30	...
Sulfur, percent by weight	0.03	0.01	0.01	0.07	0.02	0.01	...
Acid heat, °F	...	13.5	...	...	...	24	...
ASTM gum	...	0	...	...	...	0	...
Copper-dish gum, mg. per 100 ml.	...	1	...	...	...	1	...
Oxygen-bomb induction period, hours	10+	10+	...	...	...	10+	...
Reid vapor pressure, lb. per sq. in.	2.4	7.0	0.1	...	...	7	...
U. S. Navy accelerated gum	1.1	1.1	...	...	...	1.1	...
Doctor test	Sour	Slightly sour	...	...	...	Slightly sour	...
Copper-strip test	OK	OK	...	...	...	OK	...
Freezing point, °F	...	OK at —76°	...	...	...	OK at —76°	...
Octane No., ASTM motor method	57.2	77.6	70.9	...	34.7	77.7	...
After addition of tetraethyl lead: 3 ml. per gal.	...	90.5	...	...	...	92.5	...
After addition of tetraethyl lead: 6 ml. per gal.	...	95.0	...	...	...	96.0	...

* The gasolines whose properties are given in this and subsequent tables dealing with Houdry processing are raw, as condensed and stabilized, without further treatment.

a process for the production of aviation gasoline characterized by:

1. A product of high octane number—77 to 79 ASTM motor method (Table 2).
2. A product of high lead susceptibility—giving with 3 ml. of lead an octane increase to 90-93, with 6 ml. to 95-96 (Table 2).
3. A product with an acid heat of 15 °F., with treating loss of 0 to 3 percent.
4. A product with stable anti-knock property under the most severe engine conditions (Table 4).
5. Ability to produce superior aviation and motor fuels from a wide variety of charging stocks in "once-through" operation:
   a. Aviation fuel from naphthas in yield of from 30 to 60 percent (Table 1).
   b. Motor fuel from naphthas in yield of from 83

to 94 percent, requiring from 0 to 1.5 ml. of lead to give an ASTM octane number of 75 (Table 7).

c. 80-octane aviation and motor fuels from gas oils ("once-through" operation) in yields: aviation 35 to 40 percent; motor, 50 to 56 percent (Table 8).

6. Making available important increases in potential supply of high-octane aviation gasoline due to requiring greatly-decreased amounts of *iso*octanes for a given octane product as compared to straight-run aviation-base gasoline (Table 6).
7. Experience in equipment requirements and process operation on a large scale as a commercial and technical background.

TABLE 3
Typical Analysis of Dry Gas

Gas	Percent by Volume
Hydrogen	5.4
Methane	9.9
Ethene-ane	6.1
Propene	6.1
Propane	20.8
*Iso*butane	5.0
*Iso*butene	0.5
*n*Butene	3.3
*n*Butane	42.9
Pentanes+	0.0
	100.0
Specific gravity	1.565

TABLE 4
Octane Stability under Severe Engine Conditions

	ASTM Motor Method	U. S. Army Method	Supercharged-Engine Tests: 900 R.P.M. 212°F	Supercharged-Engine Tests: 1,800 R.P.M 350 to 400 °F.
Benzene*	100+0.6 ml.	88	100+6 ml.	100+0.5ml. —95
Straight-run gasoline:				
After addition of tetraethyl lead: 3 ml. per gal.	88.3	90.2	88	92
After addition of tetraethyl lead: 4 ml. per gal.	90.3	92.2	90	95
After addition of tetraethyl lead: 6 ml. per gal.	93.2	95.5	93	97
Houdry cviation gasoline:				
After addition of tetraethyl lead: 3 ml. per gal.	89.8	91.6	94	93
After addition of tetraethyl lead: 4 ml. per gal.	91.6	93.5	98	96
After addition of tetraethyl lead: 6 ml. per gal.	94.2	97.0	99.5	99

* Heron and Beatty, *J. Aeronautical Sci.* 5, 469 (1938).

TABLE 5
Analysis of Samples of Houdry Aviation Fuel

Type of Charging Stock	Paraffinic	Naphthenic
Specific gravity at 60°F	0.685	0.722
ASTM Distillation, in °F.:		
Initial boiling point	80	88
10-percent point	110	128
50-percent point	165	192
90-percent point	255	255
End point	298	298
Acid heat, °F	20	20
*n*Paraffins, percent	17	12
*Iso*paraffins, percent	63	47
Naphthenes, percent	7	25
Aromatics, percent	9	13
Olefins, percent	4	3

TABLE 6
Blending with Commercial *Iso*octane

	Percent of Commercial *Iso*octane Necessary to Blend to 100-Octane U. S. Army Method		
Tetraethyl lead per gallon, ml.	3	3.75	4
Houdry aviation	30	23	20
Straight-run aviation	50	..	..

TABLE 7
Reforming Naphtha to Produce Motor Fuel

	Grade "B" Coastal Naphtha	East Texas Naphtha	Wast Texas Naphtha
Rate of charge to catalyst, liquid volume of oil per volume of catalyst	2.25	2.0	3.8
Inspection of Charge			
Gravity, deg. API	46.8	50.4	59.2
ASTM Distillation, in °F.:			
Initial boiling point	154	245	110
10-percent point	224	268	170
50-percent point	334	308	250
End point	464	413	414
Sulfur, percent by weight	0.03	0.02	0.21
Octane No., ASTM motor method	57.2	43.4	53.2
After addition of tetraethyl lead: 1 ml. per gal.	67.8	51	61.3
After addition of tetraethyl lead: 3 ml. per gal.	76.0	64	69.0
After addition of tetraethyl lead	...	70.5(6 ml.)	71.4(4 ml.)
Yields			
Total liquid, percent by volume	92.5	94.1	95.1
Gasoline, percent by volume	83.4	90.4	93.6
Inspection of Gasoline:			
Gravity, deg. API	57.8	57.5	63.0
Initial boiling point, °F	104	94	96
10-percent point, °F	160	166	136
50-percent point, °F	256	284	227
90-percent point, °F	352	358	324
End point, °F	392	390	383
Octane No., ASTM motor method	76.5	61.8	63.5
After addition of tetraethyl lead: 1 ml. per gal.	83.5	72.4	73
After addition of tetraethyl lead: 1.5 ml. per gal.	85.1	74.5	75.2
After addition of tetraethyl lead: 3 ml. per gal.	88.5	79.9	80
Reid, vapor pressure, lb. per sq. in.	10	11	9
Sulfur, percent by weight	0.01	0.01	0.01
Color, Saybolt	30	30	30
Copper-dish gum, mg. per 100 ml.	1	1	4
Oxygen-bomb induction period, hours	10+	10+	10+

TABLE 8
Cracking Gas Oils (Once-through Operation)

Charge to Catalyst	East Texas Gas Oil	Grade "B" Coastal Gas Oil
Inspection of Charge		
Gravity, deg. API	35.7	30.9
ASTM Distillation, in °F.:		
Initial boiling point	440	424
50-percent point	534	550
End point	724	734
Yields Producing Aviation Gasoline		
Aviation gasoline, percent by volume of charge	34.9	40.2
Motor naphtha (80-octane ASTM motor method), percent by volume of charge	10.4	11.7
Catalytic gas oil, percent by volume	39.1	34.8
Gas, percent by weight	14.9	13.1
Catalyst deposit, percent by weight	5.4	5.8
Yields Producing Motor Gasoline		
Motor gasoline, percent by volume	50.2	55.8
Catalytic gas oil, percent by volume	39.1	34.8
Gas, percent by weight	11.4	10.6
Catalyst deposit, percent by weight	5.4	5.8
Aviation Gasoline		
Gravity, deg. API	63.6	62.9
ASTM Distillation, in °F.:		
Initial boiling point	111	115
50-percent point	196	204
90-percent point	288	285
End point	336	344
Acid heat, °F	40	28
Octane No., ASTM motor method	80.6	80.1
After addition of tetraethyl lead: 3 ml. per gal.	91.1	92.2
After addition of tetraethyl lead: 6 ml. per gal.	95.0	96.8
Sulfur, percent by weight	0.01	0.01
Reid vapor pressure, lb. per sq. in.	6.4	6.7
Copper-dish gum, mg. per 100 ml.	1	2
U. S. Navy accelerated gum	2.5	6.5
Oxygen-bomb induction period, hours	10+	10+
Motor Gasoline		
Gravity, deg. API	64.4	59.3
ASTM Distillation, in °F.:		
Initial boiling point	92	95
10-percent point	112	132
50-percent point	209	238
90-percent point	340	350
End point	390	413
Sulfur, percent by weight	0.01	0.01
Reid vapor pressure, lb. per sq. in.	10	10
Copper-dish gum, mg. per 100 ml.	3	3
Oxygen-bomb induction period, hours	10+	10+
Octane No., ASTM motor method	80.9	80.5
After addition of tetraethyl lead: 3 ml. per gal.	90.1	90.2
After addition of tetraethyl lead: 6 ml. per gal.	93.7	93.7

The Regeneration Step *In the* SOLUTIZER PROCESS *for the* Extraction of Mercaptans

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THE solutizer process achieves complete sweetening of sour gasolines by extracting them with caustic solutions that contain a suitable organic solvent or salt which acts as a solubility promoter, i. e., a solutizer. The spent solutized caustic solution is regenerated by stripping with steam, and can be used indefinitely to sweeten further quantities of gasoline. The present paper presents values of K_s the stripping constant, for the various pure mercaptans, and shows the calculation of the steam requirement in the regeneration of the spent solutizer solution. Such calculations are of value in helping to establish the optimum design and operating conditions of a given solutizer plant.

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TREATMENT of sour gasolines with aqueous caustic solutions, in general, does not remove the mercaptans completely enough to produce doctor-sweet products; because the heavier mercaptans are very difficult to extract. Previous work[1] has shown that this is to be attributed to the fact that the partition of the *unneutralized* mercaptan in the aqueous-caustic phase drops off markedly as the molecular weight increases. In order to counteract this effect, the solvent power of the aqueous-caustic phase was improved by incorporating therein certain organic solvents or salts which we have called solutizers. The resulting solutized caustic solutions are greatly superior to ordinary caustic solutions for extracting mercaptans, and are capable of readily sweetening most gasolines by virtually complete removal of the mercaptans.

A large number of materials have been tested as solutizers, and several have been found to be suitable for commercial-scale operation: of these the salt of *iso*butyric acid is outstanding. The results of a pilot-plant study using the *iso*butyrate solutizer have been presented previously.[2] Essentially the gasoline was sweetened by contacting it countercurrently with solutizer solution through a system of mixing and settling stages, but since that time a packed tower has been used successfully for the extraction step. The spent solutizer solution then is regenerated by stripping with steam, and can be used indefinitely to sweeten further quantities of gasoline. The process is thus a simple cyclic one, comprising an extraction and a stripping (regeneration) step.

The extraction constant, Kq, controls the extent of the extraction of a given mercaptan from a gasoline under fixed conditions and, similarly, the stripping constant, K_s, governs the regeneration of the spent solutizer solution. We have presented previously values of Kq for various pure mercaptans with ordinary and solutized caustic solutions, and an equation showing how these might be employed to calculate the extent of mercaptan removal under specified conditions.[1,2] The present paper presents values for K_s, the stripping constant, and indicates their use in calculating the steam requirement in the regeneration of the spent solutizer solution.

† The modification consisted essentially in titrating the caustic solution in the presence of 0.05N ammonium hydroxide.[4]

DETERMINATION OF K_s, THE STRIPPING CONSTANT

K_s is defined as the ratio of the moles of mercaptan per liter of steam (volume of steam measured as condensed liquid water at 20° C.) to the moles of mercaptide per liter of caustic solution (volume also measured at 20° C.).

The experimental procedure for obtaining K_s for the various pure mercaptans was as follows: The caustic solution containing the mercaptan in question was distilled without reflux from a well-insulated flask and fresh water was added back to the kettle at the same rate at which it was distilled off. In this way, the solutizer and hydroxide concentrations of the solution were kept constant during the steaming procedure. From time to time a sample of the caustic solution was withdrawn from the flask and analyzed for mercaptan, using a modification † of the silver-nitrate potentiometric titration.[3]

By making a differential material balance, one obtains an equation analogous to that for a first-order reaction, i.e.:

$$K_s = \frac{2.303}{v} \log\left(\frac{a}{a-x}\right) \qquad (1)$$

Where:

v = the volume fraction distilled, based on the volume of the kettle charge,
a = the mercaptide concentration of the original caustic solution,
a—x = the mercaptide concentration of the stripped caustic solution (after distillation of volume fraction v).

A plot of the logarithm of the mercaptide concentration

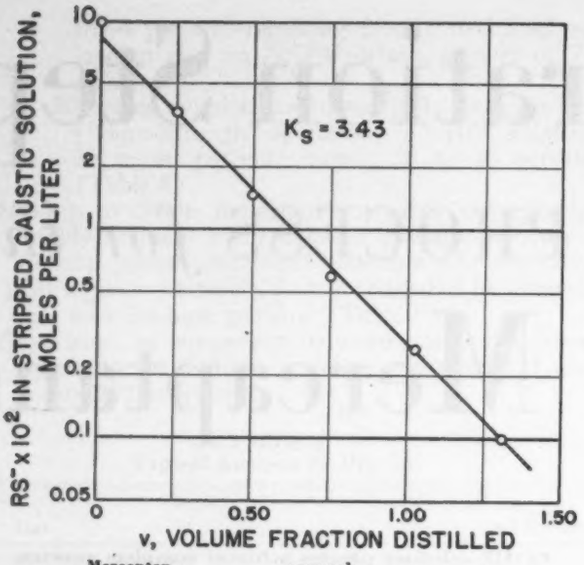


FIGURE 1

Typical Mercaptan-Stripping Curve

of the stripped caustic solution vs. the volume fraction distilled, accordingly, will yield a straight line if K_s is constant over the mercaptide range in question. This was found to be true for the various pure mercaptans, but naturally not for a mixture of mercaptans. The value of K_s selected from a run was obtained from the slope of the straight line drawn through the experimental points, rather than from experimental point-pairs. Figure 1 is a typical stripping curve. The initial point is not given as much weight as the other points, because some refluxing and some oxidation (due to dissolved oxygen) occur during the heating up of the caustic solution. K_s values greater than about 5 and less than about 0.2 are subject to considerable experimental error, unless the volume of the initial caustic charge greatly is modified; intermediate K_s values are subject to errors of the order of about 10 percent or less.

K_s can be determined experimentally in other ways, such as by the gas-flow method employed by Crary and Holm[5] in their investigation of aqueous-caustic solutions. The present method has the advantage of simplicity and of ease of operation, and is not affected by the distillation rate if refluxing or superheating of the liquid is avoided. It goes without saying that accurate mercaptide analyses are required.

TABLE 1

Summary of K_s Values for K-2 Solutizer Solution (6N KOH, 3N KIB), Undiluted and Diluted with Water Prior to Steaming

Pressure = 1 Atmosphere

	K_S							
	K-2 Undiluted Steaming Temperature = 130 to 131 °C.		K-2 Plus ½ Volume of Water, Steaming Temperature = 114 °C.		K-2 Plus 1 Volume of Water, Steaming Temperature = 108 to 109 °C.		K-2 Plus 1½ Volume of Water Steaming Temperature = 106°C.	
Mercaptan	Exceptional	Calculated	Exceptional	Calculated	Exceptional	Calculated	Exceptional	Calculated
Methyl	0.24	0.23	0.40	0.425	0.63	0.62	0.82	0.815
Ethyl	0.66	0.66	1.09	1.11	1.69	1.56	2.02	2.01
nPropyl	1.05	1.05	1.94 2.31	2.27	3.43	3.49		
Isopropyl	1.77	1.65	4.00	3.49		5.33		
nButyl	1.22 1.30 1.38	1.21	(2.63)	3.81	6.0	6.41		
Isobutyl	1.88	1.91	6.1 5.9	5.91	10 ±	9.91		
Secondary butyl		3.02		9.12		15.2		
Tertiary butyl	5.0	4.81	13.5 ±	14.1		23.3		
nAmyl	1.17 1.02	1.11	4.6 4.7[6]	4.66		8.21		
Isoamyl	1.45	1.76	5.3	7.36		13.0		
Neopentyl		4.42		17.5		30.6		
Tertiary amyl	10 ±	11		41.5		72		
nHeptyl	0.64	0.64	5.1	5.09		9.54		
nLauryl	0.13							

VALUES OF K_s

A summary of the experimental values of K_s is presented in Table 1 for the various pure mercaptans for K-2 solutizer solution [6N potassium hydroxide, 3N potassium *iso*butyrate (6N KOH, 3N KIB)] undiluted and diluted with water prior to steaming. These data were obtained by different operators over a period of about two years. The variation of K_s in duplicate runs and from the calculated values is due in part to slight differences in the composition of the various batches of solutizer solutions used, as well as to the experimental error involved in carrying through the steaming procedure.

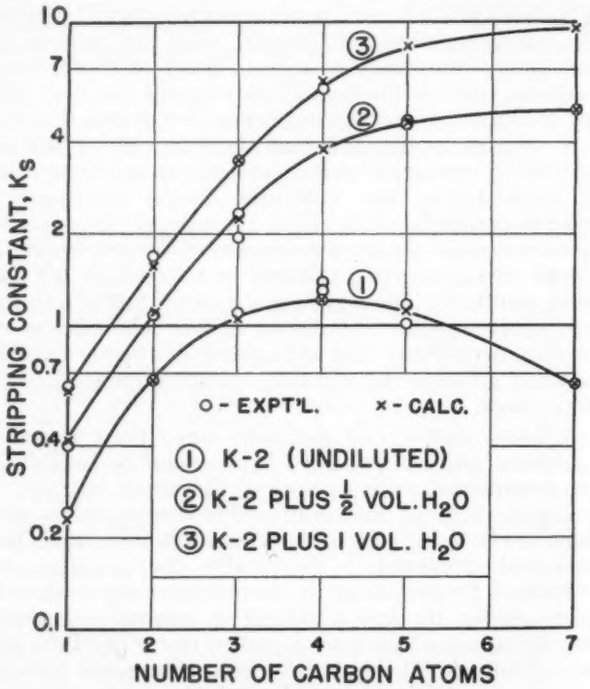


FIGURE 2

Values of K_s, the Stripping Constant, for the Various Normal Mercaptans for K-2 Solutizer Solution (6N KOH, 3N KIB), Undiluted and Diluted with Water.

The calculated values shown in Table 1 were derived from an equation expressing K_s as a function of the extent of dilution of the solutizer solution, i.e.:

$$K_s^* = aW + K_s \qquad (2)$$

Where:

K_s^* = the stripping constant of the diluted solutizer solution.
K_s = the stripping constant of the undiluted solutizer solution (in this case, K-2).
a = a constant depending on the mercaptan.
W = the extent of dilution of the solutizer solution,

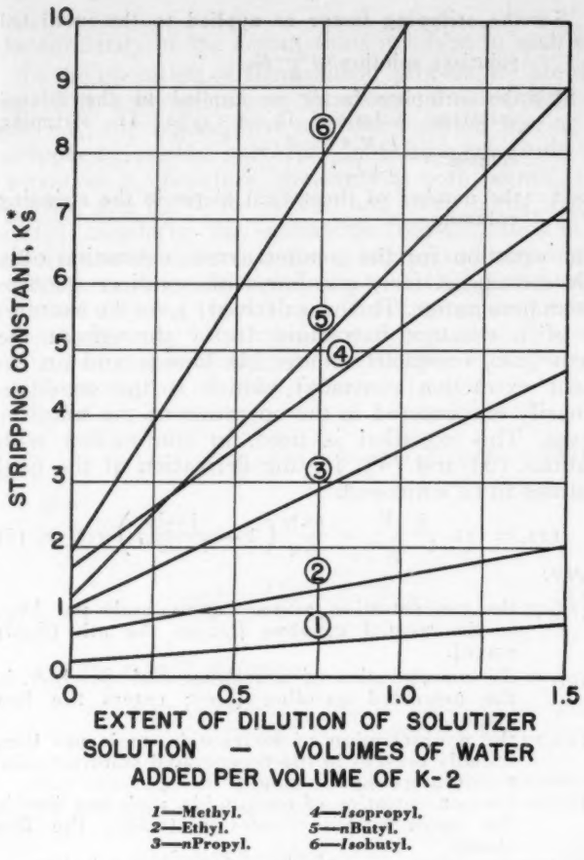


FIGURE 3

Effect of Dilution of Solutizer Solution on the Stripping Constant, K_s^*, for Several Mercaptans

i.e., the volume of water added per unit volume of solutizer (when $W = O$, $K_s^* = K_s$).

Values of a and of K_s for use in the above equation are presented in Table 2. These were obtained by smoothing the following plots:

1. log K_s vs. the number of carbon atoms in the mercaptan for K-2 solutizer and for the diluted solutions,
2. log a vs. the number of carbon atoms in the mercaptan for K-2 solutizer and for the diluted solutions, and
3. K_s (or K_s^*) vs. W.

Figure 2 shows the K_s values for K-2 solutizer and two diluted solutions as a function of the number of carbon atoms in the normal mercaptan. It is seen that K_s passes through a maximum for the K-2 solution as the number of carbon atoms in the mercaptan increases,

TABLE 2

Values of the Constants for the Equation: $K_s^* = aW + K_s$ for K-2 Solutizer and for Solutions Obtained by Diluting it with Water

Mercaptan	a	K_s
Methyl	0.39	0.23
Ethyl	0.90	0.66
nPropyl	2.44	1.05
Isopropyl	3.68	1.65
nButyl	5.2	1.21
Isobutyl	8.0	1.91
Secondary butyl	12.2	3.02
Tertiary butyl	18.5	4.81
nAmyl	7.1	1.11
Isoamyl	11.2	1.76
Neopentyl	26.2	4.42
Tertiary amyl	61	11
nHeptyl	8.9	0.64

but rises more or less continuously (or the maximum is shifted greatly) for the two diluted solutions. It is evident that the increase in K_s upon dilution of the solutizer with water is very much greater for the heavier than for the lighter mercaptans. This is illustrated further in Figure 3 for several mercaptans, where K_s^* is shown as a function of the extent of the dilution of the solutizer solution. It may be noted that the slopes of the curves of Figure 3 are equivalent to the values of a listed in Table 2.

The effect of branching of the alkyl group of the mercaptan is to increase K_s by an apparently constant

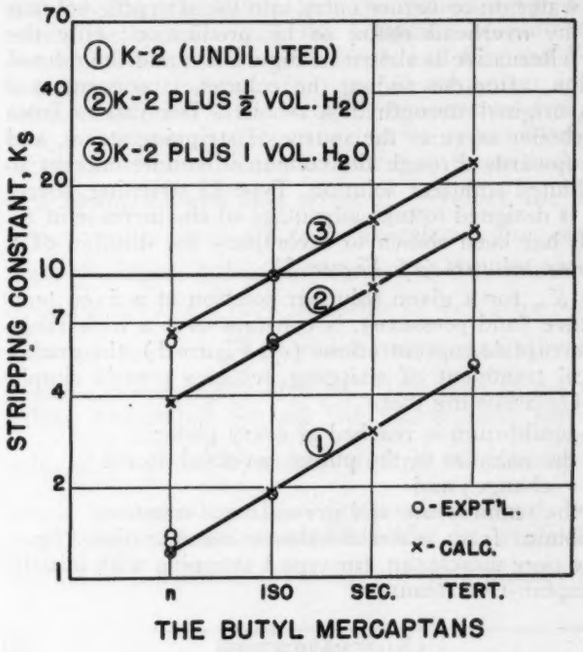


FIGURE 4

Effect of Branching of the Mercaptan on the Stripping Constant, K_s, for K-2 Solutizer Solution (6N KOH, 3N KIB), Undiluted and Diluted with Water.

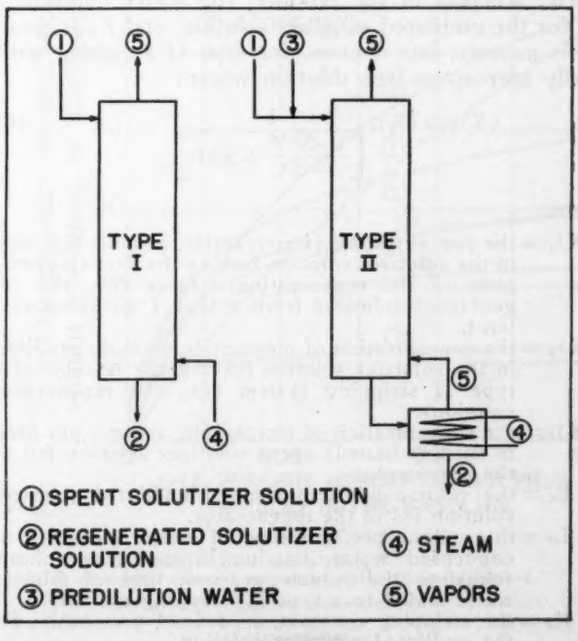


FIGURE 5

Schematic Representation of Stripping Arrangements for the Regeneration of Spent Solutizer Solutions

factor for each shift of a carbon atom, analogous to the decrease in Kq previously observed.[2] This is illustrated in Figure 4 for the butyl mercaptans only, but the propyl and amyl mercaptans behave in a similar manner.

EQUATIONS AND METHODS OF CALCULATION

Two methods for the regeneration of spent solutizer solutions will be considered, and these are illustrated schematically in Figure 5. In the first case (type I stripping), the spent solutizer solution flows in simple countercurrent to injected steam. In the second case (type II stripping), the solutizer solution is diluted with water on or before entry into the stripping column (i.e., by overhead reflux or by predilution; only the latter alternative is shown in Figure 5); and the diluted solution, after descending the column, is concentrated to its original strength in a reboiler. The vapors from the reboiler serve as the source of stripping steam, and pass upwards through the column in countercurrent to the diluted solutizer solution. Type II stripping, therefore, is designed to take advantage of the increase in K_s which has been shown to accompany the dilution of a solutizer solution (*cf.* Figure 3).

As K_s, for a given solutizer solution at a fixed temperature (and pressure), is constant over a wide range of mercaptide concentrations (*cf.* Figure 1), the mathematical treatment of stripping becomes greatly simplified. On assuming that:

a. equilibrium is reached at every plate;
b. the volumes of the phases involved do not change; and
c. the temperature and pressure are constant,

we obtain, from material-balance considerations for a single pure mercaptan, for type I stripping with initially mercaptan-free steam:

$$(X)_1 = (X)_t \frac{1-S}{1-S^{t+1}} \tag{3}$$

For type II stripping, assumptions (b) and (c) above are modified to the extent that, in the column itself, the temperature and volume relations are considered those for the diluted solutizer solution, in which case K_s* is applied; whereas in the reboiler, the above conditions hold for the undiluted solutizer solution, and K_s is used. In this manner, one obtains, for type II stripping with initially mercaptan-free dilution water:

$$(X)_R = (X)_t \frac{1}{\left[\frac{1-S^{*t+1}}{1-S^*} + SS^{*t}\right]} \tag{4}$$

Where:

$(X)_1$ = the concentration of mercaptide, as mols per liter, in the solutizer solution leaving the first (bottom) plate of the regenerating column (i.e., the regenerated solutizer from a type I stripping system).

$(X)_R$ = the concentration of mercaptide, as mols per liter, in the solutizer solution leaving the reboiler of a type II stripping system (i.e., the regenerated solution).

$(X)_t$ = the concentration of mercaptide, as mols per liter, in the (undiluted) spent solutizer solution fed to the regenerator.

L_t = the volume per unit time of undiluted solutizer solution fed to the regenerator.

L_r = the volume per unit time of steam, measured as condensed water, passing through the column (equal to the volume per unit time of dilution water added to a type II stripping system).

K_s = the stripping constant, as defined previously, for the undiluted solutizer solution.

K_s* = the stripping constant, as defined previously, for the diluted solutizer solution (applies to type II stripping only).

S = the stripping factor as applied to the undiluted solutizer solution $= \frac{L_r}{L_t} K_s$.

S^* = the stripping factor as applied to the diluted solutizer solution in a type II stripping column $= \frac{L_r K_s^*}{L_r + L_t}$.

t = the number of theoretical plates in the stripping column.

The equation for the countercurrent extraction of a single mercaptan from gasoline with solutizer solution is given hereinafter. This was derived: 1, on the assumption of a constant extraction factor throughout the system (i.e., completely-immiscible liquids and an invariant extraction constant), which is the condition ordinarily encountered in the operation of the solutizer process. This equation is used, in conjunction with equations (3) and (4), for the derivation of the final equations to be employed.

$$(z)_n = (z)_t \frac{1-E}{1-E^{n+1}} + \frac{(x)_t}{Kq}\left(1 - \frac{1-E}{1-E^{n+1}}\right) \tag{5}$$

Where:

$(z)_n$ = the concentration of mercaptan, mols per liter, in the treated gasoline [leaves the nth (final) stage].

$(z)_t$ = the concentration of mercaptan, mols per liter, in the untreated gasoline (feed; enters the first stage).

$(x)_t$ = the concentration of mercaptide, mols per liter, initially present in the regenerated solutizer solution (enters the nth stage).

$(x)_1$ = the concentration of mercaptide, mols per liter, in the spent solutizer solution (leaves the first stage).

e = the volume per unit time of solutizer solution.

r = the volume per unit time of gasoline.

$$Kq = \frac{\text{mercaptide concentration in the solutizer phase, mols per liter}}{\text{mercaptan concentration in the gasoline phase, mols per liter}}$$

E = the extraction factor $= \frac{e}{r} Kq$.

n = the number of theoretical extraction stages.

Equation (5) may be simplified to the approximate form:

$$(z)_n = (z)_t \frac{1-E}{1-E^{n+1}} + \frac{(x)_t}{Kq} \tag{6}$$

and this approximation is very closely valid for solutized caustic solutions in the range considered.

Equation (6) may be written as:

$$(z)_n = (z)'_n + (z)''_n \tag{7}$$

Where:

$(z)_n$ = the mercaptan concentration in the treated gasoline.

$(z)'_n$ = that portion of the mercaptan concentration in the treated gasoline which would be obtained by extracting with an entirely-fresh solutizer solution, i.e., initially containing no mercaptide.

$(z)''_n$ = that portion of the mercaptan concentration in the treated gasoline due to incomplete regeneration of the solutizer solution, i.e., the so-called "re-entry value."

Hence:

$$(z)'_n = (z)_t \frac{1-E}{1-E^{n+1}} \tag{8}$$

and

$$(z)''_n = \frac{(x)_t}{Kq} \tag{9}$$

It may be noted here that equation (3) for type I stripping has the same form as equation (8), due to

the similarity of the assumptions involved in each case.

In the operation of the solutizer process, we are dealing with a completely cyclic extraction-stripping system, i.e., the regenerated solutizer solution leaving the stripper enters the extractor, and the mercaptide concentration is, therefore, the same at both points $[(x)_t = (X)_1$ and $(X)_n$, for types I and II stripping, respectively]. Similarly, the mercaptide concentrations in the solutizer solution leaving the extractor and entering the regenerator are also equal $[(x)_1 = (X)_t]$. Equations (3) and (4) for types I and II stripping, respectively, accordingly may be combined with equation (9), with the aid of the auxiliary material-balance equation for a single mercaptan over the extractor, i.e.:

$$\frac{e}{r}\left[(x)_1-(x)_t\right]=\left[(z)_t-(z)_n\right]=(z)_t \qquad (10)^*$$

to give

for type I stripping:

$$(z)''_n=\frac{(z)_t}{E}\,\frac{\dfrac{1-S}{1-S^{t+1}}}{1-\dfrac{1-S}{1-S^{t+1}}} \qquad (11)$$

and for type II stripping:

$$(z)''_n=\frac{(z)_t}{E}\,\frac{1}{\left[\dfrac{1-S^{*t+1}}{1-S^*}+SS^{*t}-1\right]} \qquad (12)$$

For the case of infinite stripping plates, equation (11) for type I stripping becomes:

$$\text{when } S<1:\quad (z)''_n=\frac{(z)_t}{E}\,\frac{1-S}{S} \qquad (13)$$
$$t=\infty$$

$$\text{when } S>1:\quad (z)''_n=0 \qquad (14)$$
$$t=\infty$$

Similarly, for equation (12) for type II stripping:

$$\text{when } S^*<1:\quad (z)''_n=\frac{(z)_t}{E}\,\frac{1-S^*}{S^*} \qquad (15)$$
$$t=\infty$$

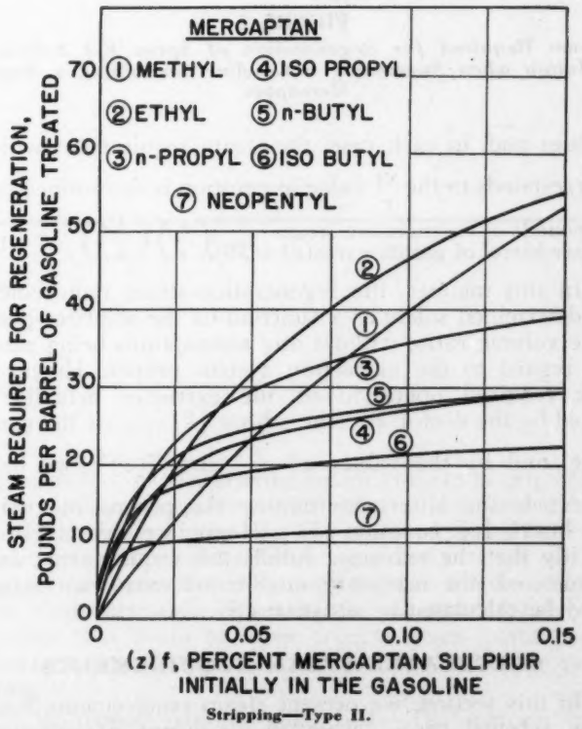
$$\text{when } S^*>1:\quad (z)''_n=0 \qquad (16)$$
$$t=\infty$$

Although all concentrations have been defined previously as mols per liter, it is evidently permissible in equations (8), (11), (12), (13), and (15) to use the more convenient units of "percent mercaptan sulfur by weight." In equation (9), however, a correction factor for the density of the oil and the aqueous phases first must be applied.

Equations (11) and (12) for type I and type II stripping, respectively, conveniently may be used together with equation (8) to calculate all the necessary relations for the solutizer sweetening of a gasoline of known mercaptan composition in a combined extraction-stripping system. For example, they may be applied to the determination of optimum operating conditions for minimum steam consumption.

Some typical calculations have indicated, for example, that—other things being equal—the steam requirement approaches a minimum when operating conditions are so adjusted that $\Sigma(z)'_n = \Sigma(z)''_n$†, i.e., when the total amount of mercaptan left unextracted by the solutizer is approximately equal to that which is re-entered because of incomplete regeneration. For our calculations, we have assumed that a gasoline containing 0.0004 percent mercaptan sulfur by weight $[\Sigma(z)_n]$ is sweet to the doctor test. This is true for most gasolines, although deviations on both sides of the above value have been observed occasionally. It, therefore, will be advisable, in general, to operate the extraction-stripping system in a manner such that $\Sigma(z)'_n = \Sigma(z)''_n = 0.0002$ percent mercaptan sulfur by weight.

The steam requirement for the sweetening of a gasoline of known initial mercaptan composition, under various conditions of operation, is calculated in the following manner. Certain constants for each mercaptan, of course, must be known for the conditions selected. These include $(z)_f$ in the gasoline feed; Kq between the gasoline and the solutizer solution at the extraction temperature considered; and K_s (and $K_s{}^*$ as a function of dilution, for type II stripping) for the solutizer solution at the stripping temperature and pressure. Furthermore, we must select the type of stripping which is to be used and the number of theoretical stripping plates, as well as a series of $\frac{e}{r}$-values for which steam requirements are to be calculated. For each of these $\frac{e}{r}$-values, it then is necessary to determine [from equation (11) or (12)] the value of $(z)''_n$ for various assumed values of $\frac{L_r}{L_f}$, for each mercaptan in the initial gasoline. From a plot of $\Sigma(z)''_n$ [the sum of the $(z)''_n$ values calculated for all the mercaptans for each value of $\frac{L_r}{L_f}$] vs. $\frac{L_r}{L_f}$, we may pick off the value of $\frac{L_r}{L_f}$ which corresponds to the $\Sigma(z)''_n$ value desired, in this case 0.0002 percent mercaptan sulfur by weight. This method of calculation is carried out for a number of $\frac{e}{r}$



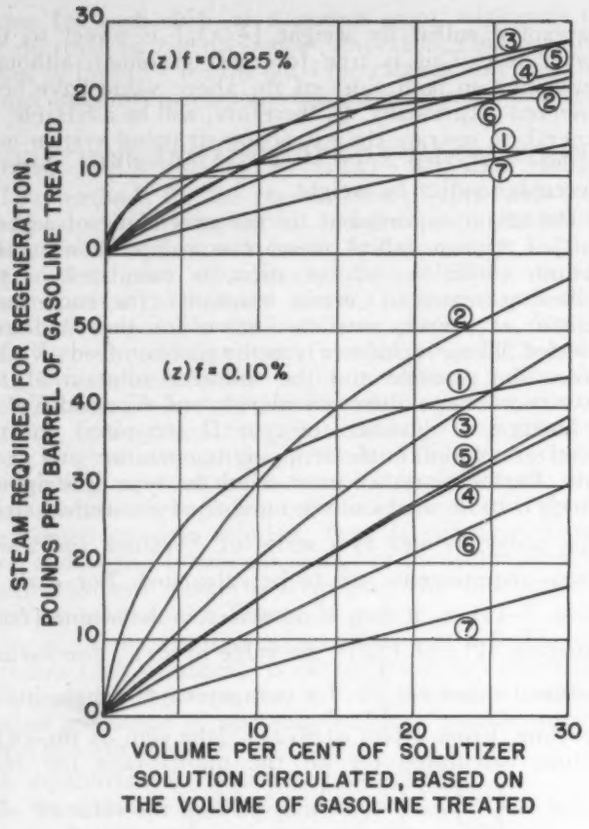
Stripping—Type II.
t—10 (theoretical column plates).
$(z)''_n$—0.0002 per cent mercaptan sulfur (re-entry values).
$\frac{e}{r}$—0.20 (solutizer-gasoline volume ratio).

FIGURE 6

Steam Required for Regeneration of Spent K-2 Solutizer Solution when Sweetening a Gasoline Containing a Single Mercaptan.

* The approximation that, for a given mercaptan, $[(z)_f-(z)_n]$ is equal to $(z)_f$ is generally quite valid when a doctor-sweet gasoline is to be produced, because $(z)_n$ then must be extremely small.

† The symbol Σ is used to denote the total concentration of all mercaptans in the phase in question.


(z)f=0.025%
(z)f=0.10%
STEAM REQUIRED FOR REGENERATION, POUNDS PER BARREL OF GASOLINE TREATED
VOLUME PER CENT OF SOLUTIZER SOLUTION CIRCULATED, BASED ON THE VOLUME OF GASOLINE TREATED

Stripping—Type II.
t—10.
$(z)''_n$—0.0002 per cent mercaptan sulfur (re-entry value).
$(z)f$—indicated in figure (mercaptan sulfur initially in the gasoline).

Mercaptan: 1—Methyl. 2—Ethyl. 3—*n*Propyl. 4—*Iso*propyl. 5—*n*Butyl. 6—*Iso*butyl. 7—Neopentyl.

FIGURE 7

Steam Required for Regeneration of Spent K-2 Solutizer Solution when Sweetening a Gasoline Containing a Single Mercaptan.

values and, in each case, the steam requirement which corresponds to the $\frac{e}{r}$ value in question is determined by:

$$\text{pounds of regeneration steam per barrel of gasoline treated} = 350\left(\frac{e}{r}\right)\left(\frac{L_r}{L_t}\right) \qquad (17)$$

In this manner, the regeneration-steam requirement is determined solely as a function of the solutizer-gasoline volume ratio, without any assumptions being made in regard to the extraction system proper. However, the required operation of the extractor actually is fixed by the doctor-sweetness limit $[\Sigma(z)_n]$ of the gasoline, and by the values of $\frac{e}{r}$ and $\Sigma(z)''_n$ we have selected—the latter determining the permissible value of $\Sigma(z)'_n$ [*cf.* equation (7)]. Hence, we have assumed tacitly that the extractor fulfills this requirement; and, if desired, the necessary number of extraction stages may be calculated by equation (8).

CALCULATED STEAM REQUIREMENTS

In this section, we present steam requirements for a few selected cases calculated by means of equations (11) and (12). The values of K_s used were the smoothed ones taken from Table 1 or interpolated from plots similar to Figure 3. The values of Kq used were those listed in Table 3. It may be noted that the present Kq values are somewhat smaller than those presented before.[2] This is due to the fact that the extraction

TABLE 3

Smoothed Kq Values for the Various Mercaptans for K-2 Solutizer Solution

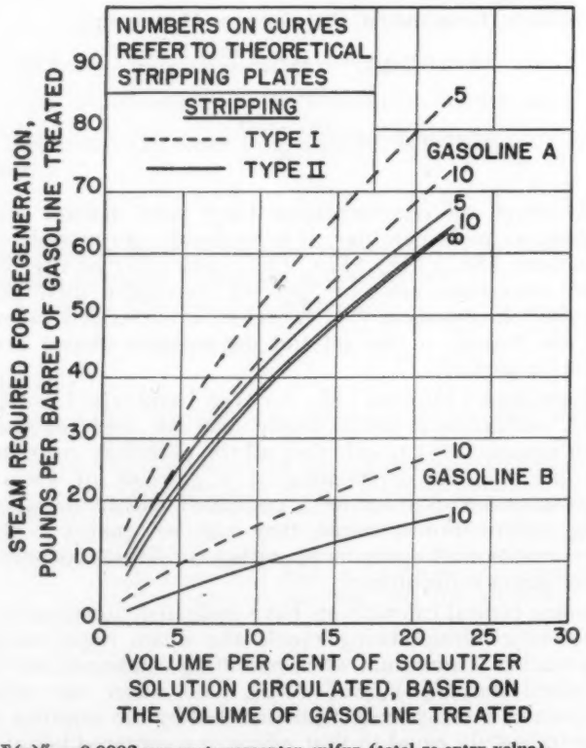
Temperature .....90° F.
Oil Phase .....Gasoline

Mercaptan	Kq	Mercaptan	Kq
Methyl	12,650	Tertiary butyl	88
Ethyl	2,480	*n*Amyl	206
*n*Propyl	765	*Iso*amyl	130
*Iso*propyl	495	Neopentyl	51
*n*Butyl	344	Tertiary amyl	20.4
*Iso*butyl	220	*n*Heptyl	146
Secondary butyl	140		

temperature considered at this time is somewhat higher than before, *i. e.*, 90 °F. instead of 20 °C.; and the oil phase is now a gasoline instead of *iso*octane.

Figure 6 shows the steam required for regeneration of the spent solutizer solution for various pure mercaptans as a function of the initial mercaptan concentration in the gasoline being treated. In this case, type II stripping was used, and the solutizer-gasoline volume ratio $\frac{e}{r}$ was maintained constant at 0.20. It will be noted that the amount of steam required is different for each mercaptan; and, as expected, increases as the initial mercaptan concentration in the gasoline increases. We may say, in general, that more steam is required for the lighter than for the heavier mercaptans under these conditions.

Figure 7 shows the effect of varying the solutizer-gasoline volume ratio $\frac{e}{r}$ for the various mercaptans at an initial concentration of 0.025 percent and 0.10 percent


NUMBERS ON CURVES REFER TO THEORETICAL STRIPPING PLATES
STRIPPING
TYPE I
TYPE II
GASOLINE A
GASOLINE B
STEAM REQUIRED FOR REGENERATION, POUNDS PER BARREL OF GASOLINE TREATED
VOLUME PER CENT OF SOLUTIZER SOLUTION CIRCULATED, BASED ON THE VOLUME OF GASOLINE TREATED

$\Sigma(z)''_n$—0.0002 per cent mercaptan sulfur (total re-entry value).
$\Sigma(z)f$—Gasoline *A*—0.36 per cent mercaptan sulfur.
Gasoline *B*—0.055 per cent mercaptan sulfur (total mercaptan sulfur initally in the gasoline).

FIGURE 8

Steam Required for Regeneration of Spent K-2 Solutizer Solution when Sweetening Gasolines Containing Mixtures of Mercaptans.

mercaptan sulfur in the gasoline. The steam required increases as the value of $\frac{e}{r}$ increases, but the extent of this is greatly dependent on the initial mercaptan concentration in the gasoline as well as on the particular mercaptan.

Figure 8 shows the steam required for two hypothetical gasolines as a function of the solutizer-gasoline volume ratio $\frac{e}{r}$. In this case, calculations were made for both type I and type II stripping, using different numbers of theoretical column plates. Gasoline **A** contained a mixture of mercaptans ranging from methyl to neopentyl, and the total initial mercaptan sulfur was 0.36 percent by weight. Gasoline **B** contained a mixture of the heavier mercaptans only, the butyls and neopentyl; and the total initial mercaptan sulfur was 0.055 percent by weight. It will be observed that the slope and magnitude of the steam curves vary greatly for these gasolines—depending on the initial mercaptan concentration and on the type of mercaptans, as noted above. It is indicated that little advantage is gained by employing more than about 10 theoretical stripping plates. As expected from the increase in K_s upon dilution with water, steam requirements are lower for type II than for type I stripping. Of particular interest is the much smaller effect of the number of theoretical plates in the case of type II stripping.

Calculations such as those shown above are of value in helping to establish the optimum design and operating conditions of a solutizer plant. Usually it is not possible to make such calculations for a specific gasoline; because its mercaptan composition, as a rule, cannot be determined with sufficient accuracy. However, from a knowledge of the total mercaptan concentration and the general type of mercaptans present (the latter of which is judged by the case of extraction of the gasoline with solutizer), a reasonable estimate of the required steam can be obtained from curves such as those shown in Figures 6 and 7. Thus, for the solutizer sweetening of a particular gasoline, the steam required for type II stripping when circulating 35 percent by volume of solutizer solution $\frac{e}{r} = 0.35$ was estimated at 20 to 30 pounds per barrel of gasoline treated. The values actually obtained when sweetening this gasoline in the pilot plant under the above conditions were 26 pounds and 29 pounds for two separate runs.

BIBLIOGRAPHY

[1] D. L. Yabroff, "Extraction of Mercaptans with Alkaline Solution," presented before Petroleum Div., *Am. Chem. Soc.*, Baltimore, Apr. (1939); to be published in *Ind. Eng. Chem.*

[2] D. L. Yabroff and L. E. Border, *Proc. API* **20M [III]** 95-103 (1939).

[3] M. W. Tamele and L. B. Ryland, *Ind. Eng. Chem.* (*Anal. Edn.*) **8**, 16-9 (1936).

[4] M. W. Tamele and L. B. Ryland, private communication.

[5] R. W. Crary and M. M. Holm, *Ind. Eng. Chem.* **29**, 1389-92 (1937).

Catalytic Desulfurization

[*Continued from page 99*]

the TEL requirement to 100 octane number was 3.4 ml. for the former and 2.7 ml. for the latter.

From the test data it is estimated that the percent *iso*octane required to just make 100 octane number with 3.0 ml. TEL was changed from 56.0 to 48.8 by desulfurization of the New Mexico straight-run gasoline. This represents an increase in 100-octane gasoline production of 14.8 percent.

It should be recalled that the New Mexico straight-run gasoline had the very low sulfur content of 0.013 percent before the bauxite-desulfurization treatment. This example, therefore, illustrates the advantages to be derived from complete desulfurization.

CONCLUSIONS

The catalytic removal of sulfur from aviation blending naphthas, even when the sulfur content is originally very low, has been shown to exert a beneficial effect on TEL susceptibility. In the case of one blending naphtha, a pentane-free natural gasoline of high sulfur content and comparatively high octane number, catalytic desulfurization increased the amount of finished gasoline that could be made from a given quantity of 91-octane commercial *iso*octane by the following percentages:

92 octane with 0.5 ml. TEL—19.7 percent
100 octane with 3.0 ml. TEL—27.7 percent
87 octane with 1.0 ml. TEL—52.2 percent

BIBLIOGRAPHY

[1] Schulze and Buell, *Oil Gas J.* **34 [28]** 36, 37, 39 (1935).

[2] Birch and Stansfield, *Ind. Eng. Chem.* **28**, 668-72 (1936).

[3] Graves, *Ind. Eng. Chem.* **31**, 850-56 (1939).

In Case of Fire

HOW to win a cavalry skirmish was once thus described: "get there fustest with the mostest men."

In a little different language the best advice for conquering a refinery fire is—get there immediately with the proper equipment.

Even that is not enough. The crew must get there with the proper equipment and with the equipment in working order.

DIRT DAUBERS AND CUP GREASE

An instance (fortunately the equipment never was called upon for fire fighting) recently came to light in connection with foam-type extinguishers. In the first place someone allowed workmen to deviate from instructions for the annual test of extinguishers. Because the resultant foam left a difficult cleaning job, the two chemicals of the extinguishers were drained into separate sewers, then refilled and put back in place under the assumption they were ready for any fire.

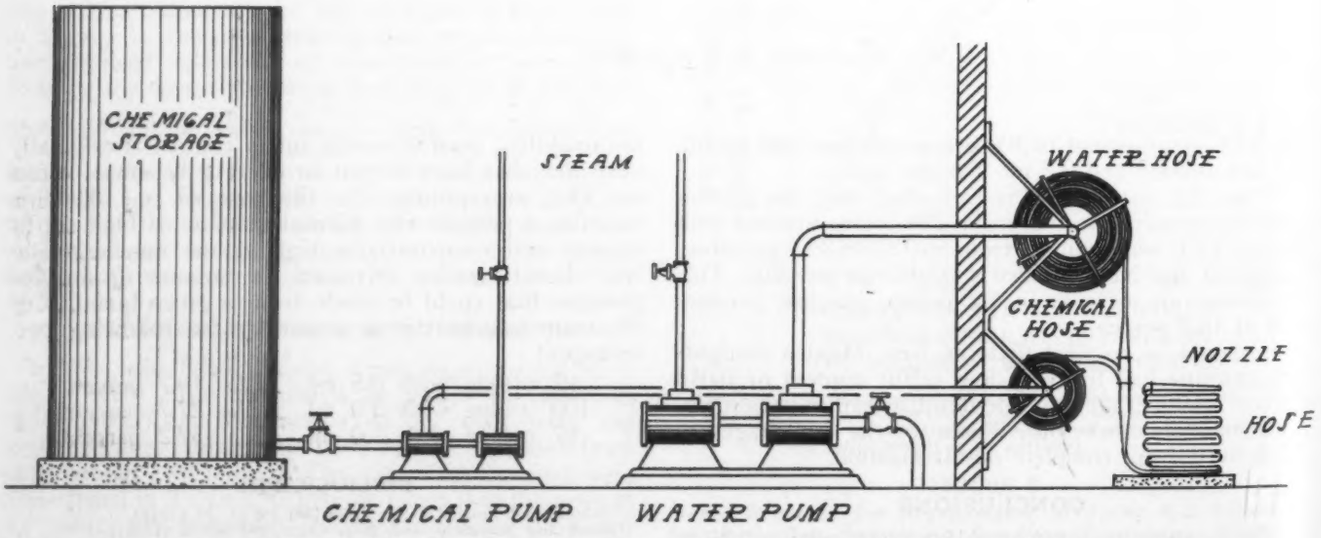
Finally a man new to the plant decided to follow instructions of the manufacturer. The nozzle of one 40-gallon extinguisher was opened but no foam responded. The bulging hose gave evidence that the chemicals were reacting.

Investigation revealed that dirt daubers had selected the nozzles for nest building. Only one extinguisher of this size was free of the obstruction and several of the smaller sizes were obstructed.

The problem was solved by inserting the nozzles in heavy cup grease with viscosity sufficient to resist highest temperatures. It was found that the plug of grease would keep the insects out but would blow out readily from chemical pressure.

SO A FEW MEN CAN DO A BIG JOB

In order to fight an oil fire effectively the fire fighting equipment must be so arranged that a few workmen can apply the chemicals to the fire in a very short time. The sketch shown, illustrates a permanent hook-up which can be operated with two men and the fire reached within one minute after it is discovered. A dual system of hose is necessary until the chemicals and water reach the V connection and from that point two lengths of 50-foot hose are used. Two lengths of single hose are necessary for the proper mixing of the chemical and water. The procedure is that one operator strings the hose while the other is starting the pumps. Any length of hose can be placed in the reels so long as the lengths are equal.



NO HOSE KINKS

Hangers for steam hose will prevent kinking regardless of the speed in getting the nozzle to the fire. This hanger is in the Garber plant of Omar Refining Company.

The hanger is made from tank steel and attached to studding of plant equipment. One man can get steam to any point within hose length by opening the globe valve and making haste to the fire with the nozzle end of the hose.

BY THEIR COLORS

Often there is much difficulty in keeping the steam fire hoses at the proper locations. There is no way of preventing them from straying to other units, especially during times of emergency use. Often the steam hose does not return to its proper location because of lack of identification.

One scheme was to place metal tags on each end of the hose. This had the disadvantages of making for difficult handling and the tags were easily removed or lost. Following this it was decided to paint a stripe of appropriate color the full length of each hose; yellow stripes for tube still and shell units, red stripes for the high-pressure cracking units, and white stripes for low-pressure cracking installation.

SAND FOR THE GROUND FIRE

Fires from spilled oil are easily controlled with sand.

An effective container for sand is the drum, with half of one end cut out and the barrel laid in concrete cradles with the open half of the end downward.

To be effective these drums must be placed near all points where oil is likely to be spilled or where connections are liable to break. In order to be quickly seen at night they should be painted in a light color and the sand supply can be preserved by lettering to designate that the sand is for fire use only.

The drum pictured is one of many at the Allen, Oklahoma, plant of Sunray Oil Company.

The Use of Gum Inhibitors in the Refining of Motor Fuels*

W. W. SCHEUMANN
Cities Service Oil Company

PRODUCTION of motor fuels for internal combustion engines by cracking of heavy or intermediate petroleum fractions, reforming of straight-run naphthas, and thermal or catalytic polymerization of gaseous hydrocarbons includes among other manufacturing requirements that the products from these operations receive a chemical treatment, in order to result in a satisfactory finished motor fuel. This chemical treatment may be conveniently be divided into two types, the first of which is a stabilizing treatment to insure stability against gum formation and loss of anti-knock value and color in storage. The necessity for this treatment is due to the fact that the raw products from cracking, reforming, and polymerization are very susceptible to deterioration when stored in contact with air. This deterioration is primarily an oxidation of unsaturated constituents to form peroxides, aldehydes, and acidic bodies, which finally through polymerization result in gums and resins.[1] Unsaturated compounds containing conjugated double bonds are the most reactive in this respect, but over long time periods even simple olefins undergo this type of oxidation. In addition to the formation of gum, a loss of anti-knock value takes place, due apparently to the effect of the peroxides which have been formed during the oxidation. A third change resulting from this deterioration is a gradual darkening of color. Apparently this is due in part to oxidation although sulfur and sulfur compounds present in the gasoline enter into the reaction and exert an accelerating influence.[2]

The second type of chemical treatment is a sweetening treatment to meet marketing demands for a doctor-sweet product of acceptable odor. Essentially this treatment consists in removing hydrogen sulfide and either removing the mercaptan sulfur compounds or converting them to the corresponding disulfides, whose ethereal odor is usually considered more pleasant than that of the mercaptans.

In instances where high-sulfur stocks are being processed, chemical treatment may also be required to reduce the sulfur content of the product to satisfactory limits. However, this reduction of sulfur content is usually accomplished simultaeously with, or as an integral part of the previously mentioned types of treatment.

TREATING METHODS

Various methods for treating gasolines of the types previously mentioned are being used by the industry today in order to secure satisfactory stability. The oldest method and the one still most widely used is sulfuric-acid treatment. This process consists of contacting the naphtha or benzine with sulfuric acid, settling and drawing off the acid sludge, washing the naphtha with water, and contacting the naphtha with either caustic soda or sodium plumbite (doctor) solution. Following this the treated naphtha is redistilled in order to recover the gasoline of desired boiling range. With proper choice and control of acid/oil ratio, acid concentration, treating temperature, degree and time of contact, thoroughness of sludge removal, thoroughness of water wash and neutralizing treatment, and temperature and degree of fractionation in the redistillation operation, this process will yield products having a good color and storage stability and which are satisfactory in every respect. However, this process is expensive and wasteful because of the loss which takes place, due to the solution of hydrocarbons in the acid, the polymerization of unsaturated compounds to high-boiling materials, and the loss incurred in redistillation. In addition to this physical loss, the hydrocarbon constituents removed are of high anti-knock value and the loss of octane number caused by this refining treatment must be compensated for by the use of additional tetraethyl of lead in the final product.

Many of these objections are overcome in several other treating methods which are used to a lesser extent. In these processes the highly unsaturated constituents are polymerized to a high-boiling polymer which is removed from the treated material by fractional distillation or condensation. Such processes include the Gray process in which fuller's earth or more properly filter clay acts catalytically in the vapor phase to cause this polymerization, the Osterstrom process in which filter clay acts catalytically in the liquid phase, the Lachman process in which zinc chloride is the polymerizing agent, and several others of a similar type. Of these processes the clay-treating type are probably in use to the greatest extent.

However, in contrast to these processes in which the product is stabilized by the removal of the unstable constituents, a newer and more economical method of treating is finding increased acceptance in which the unsaturated constituents are not removed, but are protected against oxidation by adding to the gasoline a very small amount of a substance known as a gum inhibitor or anti-oxidant.

Gum inhibitors are compounds which protect a gasoline by preferentially reacting with the oxygen dissolved in it, instead of permitting it to oxidize the fuel constituents. The development of powerful and

*Before the Western Petroleum Refiners Association, Shreveport, October 27, 1939.

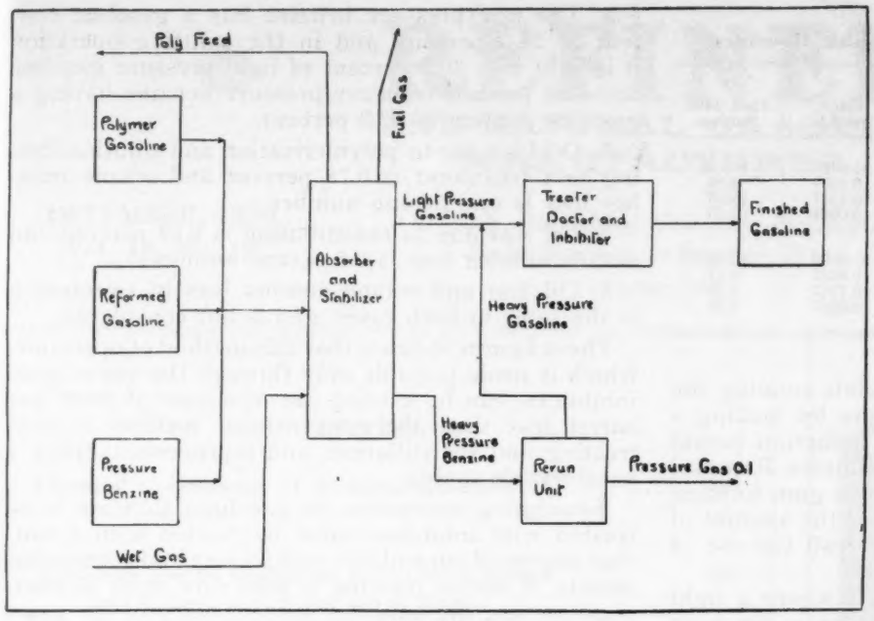


FIGURE 1

efficient inhibitors for gasolines constitutes a brilliant scientific achievement in the petroleum and allied chemical industries. Early work in this field indicated the existence of a large number of organic chemical compounds which might be added in small amounts to gasolines to inhibit oxidation. In general, these compounds were of the type containing phenolic or primary or secondary aromatic amine groupings.[3] However, while the ability to prevent deterioration of the gasoline, when used in low concentration, is the most essential requirement of a commercial inhibitor, there are several other factors which are of considerable importance. In order to be commercially satisfactory an inhibitor should be readily soluble in gasoline, it should be insoluble or very sparingly soluble in water or caustic soda solutions, it should not impart color to the gasoline, and it should be non-reactive with tetraethyl of lead and oil-soluble dyes. Many of the early compounds used were effective as far as oxidation inhibition was concerned, but were not satisfactory for commercial use because they failed to meet these other requirements. However, a large amount of research and development work carried out by various organizations has resulted in the development and offering to the trade some very effective inhibitors which meet to an excellent degree the previously mentioned requirements.

The inhibitors in general commercial use are, therefore, limited to a relatively small number of compounds including such materials as monobenzyl-para-aminophenol, dibenzyl-para-aminophenol, isopropyl monomethyl-para-aminophenol, monobutyl-para-aminophenol, mono isobutyl-para-aminophenol, and hardwood tar acids. The use of these compounds as gum inhibitors is patented, and they are sold under various trade names by the organizations marketing them, royalty charges being included in the price.

The utilization of gum inhibitors in refining operations on cracked, polymerized, or reformed stocks may be coupled with various treating methods depending upon the nature of the stocks being processed, the fractionation facilities available on the units, and final quality requirements. These may include:

1. Production of end-point and vapor-pressure material directly from the unit, sweetening and inhibiting for stability.

2. Clay treating end-point material to polymerize only the most unstable constituents, sweetening and inhibiting to a satisfactory degree of stability.

3. Using a light acid treatment on a benzine fraction followed by redistilling, sweetening the gasoline and inhibiting to a satisfactory degree of stability.

4. Splitting a benzine fraction into a light and heavy portion in connection with stabilizing operations, acid treating and redistilling the heavy fraction, sweetening the combined redistilled heavy gasoline and light gasoline, followed by inhibiting to a satisfactory degree of stability.

ECONOMIES

Method No. 1 can, of course, only be used where the material treated is produced from units equipped with suitable fractionating and stabilizing equipment, and where a water-white color of the final product is not necessary. Ordinarily this color requirement presents no problem where the final product is dyed. This method offers the greatest possibilities of savings through the use of inhibitors, since it eliminates entirely the volumetric loss suffered in acid treatment and rerunning, the cost of these operations, and the octane number loss due to the use of acid. Against these the cost of the inhibitor is very small and there exists a large net savings in expense. It has been estimated that on typical Mid-Continent type cracked stocks, this savings can amount to as much as $0.03-$0.04 per barrel of gasoline not including the reduction of volumetric loss and lead savings.[4]

The use of inhibitors in the second method also

TABLE 1

Comparative Cost Figures for Finishing Cracked Benzine Per Barrel Finished Gasoline

(a) Acid Treatment and Rerunning of Entire Benzine Fraction

1. Treating	Chemical Treatment of Benzine	$0.0095
	Oil Loss	0.0205
	Lead Equivalent to Octane Loss	0.0106
2. Rerunning	Oil Loss	0.0136
	Lead Equivalent to Octane Loss	0.0052
3. Sweetening	Chemical Cost	0.0020
	Total	$0.0614

(b) Acid Treatment and Rerunning of Heavy Fraction—Using Inhibitor in Final Product

1. Treating	Chemical Treatment of Benzine	$0.0065
	Oil Loss	0.0120
	Lead Equivalent to Octane Loss	0.0062
2. Rerunning	Oil Loss	0.0079
	Lead Equivalent to Octane Loss	0.0031
3. Sweetening	Chemical Cost	0.0020
	Inhibitor Cost	0.0023
	Total	$0.0400

TABLE 2
Variation of Inhibitor Effectiveness with Gasolines

Inhibitor	Requirements for 6 Hour Induction Period, Lbs./1000 Barrels	Price, per Lb.	Cost/1000 Barrels
GASOLINE A:			
No. 1	6.10	$1.6487	$10.06
No. 2	8.08	0.8487	6.86
No. 3	16.20	0.7387	11.96
No. 4	116.60	0.0927	10.80
GASOLINE B:			
No. 1	3.03	$1.6487	$5.00
No. 2	7.27	0.8487	6.17
No. 3	9.10	0.7387	6.72
No. 4	49.29	0.0927	4.57

offers economies since it makes possible running the clay to greatly increased throughputs by making a product of poorer initial color and induction period which can be easily handled with inhibitors. Removal of the highly unstable and most active gum-forming constituents in this manner, decreases the amount of inhibitor required, so that in the overall the use of inhibitors offers a savings in expense.

The same is true in method No. 3 where a light acid treat using weak acid removes only the most active constituents and the decreased volumetric loss and octane savings more than compensates for the cost of the inhibitor, when contrasted with complete stabilization by means of acid treatment.

These three operations have been previously described in the literature in considerable detail, however, the writer is not familiar with previous discussions of operation No. 4 and will, therefore, include the following data concerning this operation.

Several reasons exist for its use, namely the fact that distillate fuel oils must be produced from the benzine which requires acid treatment and rerunning for satisfactory stability of these products, as well as the fact that the cracking units in question are not equipped to make end-point gasoline. Figure 1 is a flow diagram of this method of processing. Unstable polymer gasoline, reformed straight-run gasoline, and cracked benzine are charged as common stock to the absorption and stabilization unit, along with the wet drum gas. Here this material is fractionated into fuel gas, polymer plant charge, light-pressure gasoline and heavy-pressure benzine. The heavy-pressure benzine is treated with sulfuric acid and caustic soda solution, and redistilled to yield heavy-pressure gasoline and distillate fuels. The light- and heavy-pressure gasolines are blended in the proportions produced, doctor treated, and inhibited for finished gasoline.

FROM PLANT EXPERIENCE

In Table 1, a cost comparison is shown for this operation, and conventional acid treatment and rerunning. In making this comparison the following items which are the result of actual plant experience are used as a basis.

1. In both cases the benzine is considered debutanized to a degree compatible with the vapor pressure required on the finished product, therefore, no gas yield is obtained on redistillation.

2. No labor costs are included, as it is assumed that the labor requirements are the same in both operations.

3. No fuel and utility costs are included, as it is assumed these are identical.

4. The induction period of the finished product is the same in both cases.

5. The raw pressure benzine has a gasoline content of 74.5 percent, and in the splitting operation it is split into 30.5 percent of light-pressure gasoline and 69.5 percent of heavy-pressure benzine having a gasoline content of 63.3 percent.

6. Oil loss due to polymerization and solution during acid treatment is 0.78 percent and octane number loss is one octane number.

7. Oil loss due to redistillation is 0.52 percent and octane number loss is 0.5 octane numbers.

8. Oil loss and octane number loss in sweetening is the same in both cases, and is not considered.

These figures indicate that this method of operation, which is made possible only through the use of gum inhibitors, can be carried out at a cost of $0.02 per barrel less than the conventional method of acid treating and redistillation, and represents thereby a considerable saving.

Sweetening operations on gasolines that are to be treated with inhibitors must be carried with a suitable degree of control, for satisfactory and economical results. If doctor treating is used care must be exercised so that the inhibitor susceptibility of the gasoline is not lowered by excess free sulfur. It has been shown that a gasoline may be sweet and noncorrosive and still contain sufficient free sulfur to very appreciably lower the initial induction period, and greatly increase the amount of inhibitor required.[5]

It is also important that a clean separation be made between the gasoline and the treating solution, since alkali reacts with the phenolic groups in the inhibitor and also acts as a catalyst for its oxidation. The gasoline should, therefore, be settled until clear and bright before the inhibitor is added.

In this connection some of the newer sweetening processes such as copper sweetening, produce a product admirably suited for inhibiting since it contains no added elementary sulfur and no caustic soda in suspension.

In making a choice of inhibitors for any particular gasoline the most economical inhibitor can only be determined as the result of experimentation. Inhibitor effectiveness varies in different gasolines, and a simple study of the relationship between improvement in induction period and inhibitor concentration may be used in making this choice. This is illustrated in Table 2, showing the relative effectiveness of four commercial inhibitors in two different gasolines. It can readily be seen that inhibitor No. 2 is the most economical inhibitor for Gasoline A, and inhibitor No. 4 is the most economical for Gasoline B.

The use of gum inhibitors in refining operations is, therefore, a modern development, which can readily be fitted into an existing scheme of operations, with little difficulty. By the use of these compounds a product of actually improved quality may be made since valuable constituents in the motor fuels are conserved. Moreover these benefits can be obtained with what every refiner is searching for, namely reduced operating costs.

BIBLIOGRAPHY

[1] Dryer, Lowry, Morrell and Egloff, Mechanism of Gum Formation in Cracked Gasoline, Ind. Eng. Chem. **26** (8), 885 (1934) August.

[2] Morrell, Benedict, Egloff, Stability of Pure Hydrocarbons to Light, Ind. Eng. Chem. **28** ( ), 448, (1936) April.

[3] Byers, J. H., The Patent Literature on Gum Inhibtors, Nat. Pet. News **29** (11) 157-160 (1937) March 17; **29** (15) 58-61 (1937) April 14.

[4] Nisson, P. S., and Ross, W. B., Economics of Treating and Inhibiting Gasoline, Oil & Gas Journal **35** (50) 56-61 (1937) April 29.

[5] Lowry, Dryer, Wirth and Sutherland, Factors in Doctor Sweetening, Industrial and Eng. Chem. **30** (11) 1275-79 (1938) Nov.